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ON THE SCATTERING OF POLARISED NEUTRONS BY PROTONS

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1. Introduction

As is well known, it has not been possible so far to develop a satisfactory theory of nuclear forces which accounts for all the properties of even the simplest nuclear system, a neutron and a proton. One has, therefore, to attempt to obtain the nuclear interaction empirically from the various observed properties, like the binding energy, quadrupole and magnetic moments of the deuteron and the scattering cross-section between neutrons and protons. Recently Bhatia (1949, 1950*) has suggested an additional property, namely, the scattering and the consequent depolarisation of a polarised beam of neutrons (or protons) by unpolarised protons (or neutrons) as a means of obtaining information about the neutron-proton interaction.

It is known from general considerations that the N–P interaction†—apart from its exchange character, the only effect of which is to make the interaction different in states of odd and even parity—must consist of two terms: (*a*) a spherically symmetrical term which is spin-dependent (*i.e.*, is different for the singlet and triplet states) and (*b*) a term which is not only a function of the distance between the two particles, but also of the angles which the spin directions of the two particles make with the line joining them (this is usually called tensor interaction).

Now (1) it is shown in (B) that if the tensor term (*b*) in the *N–P* interaction were zero, then from a knowledge of the differential scattering cross-section $\sigma(\theta)$ and the polarisation cross-section $P(\theta)$ (as functions of the angle of scattering θ) one could determine the phase-shifts both for the singlet and the triplet states for the partial wave of each orbital angular momentum l ($l=0, 1, 2\ldots$); thus reducing the problem of determining the interaction potential both for singlet and triplet states separately, to one

* In what follows this Paper will be referred to as (B), for brevity.

† A dynamic interaction will, of course, also exist. We shall assume here, however, that the static terms (*a*) and (*b*) are predominant.

already considered by Hylleraas (1948) and Fröberg (1948 *a*, *b*) for spinless particles. (2) When the tensor term (*b*) is not zero, a qualitatively new feature appears in that both $\sigma(\theta\phi)$ and $P(\theta\phi)$ depend not only on the angle of scattering θ but also on the azimuth ϕ of the scattered direction. The extent of the azimuthal dependence of $\sigma(\theta\phi)$ has been calculated for various energies of incident neutrons by Wolfenstein (1949 *b*) while that of $P(\theta\phi)$ has been calculated in (B) for low ($\sim$ 1 MEV) and very high energy neutrons with the usually assumed forces. The expected azimuthal dependence of both $\sigma(\theta\phi)$ and $P(\theta\phi)$ is found to be of comparable magnitude with their ϕ-independent terms.

In this Paper it is shown that even when the N-P interaction contains the tensor term (*b*) all the scattering parameters of the theoretical expression can be determined from a knowledge of $\sigma(\theta\phi)$ and $P(\theta\phi)$ as functions of θ and ϕ. This is of particular interest since in a recent paper Holmberg (1950) has shown that the interaction potential can be derived theoretically at least up to Fröberg's approximation in this case as well, if the parameters are known as functions of energy.

It may immediately be mentioned (*a*) that in view of recent papers by Bargmann (1949 *a* and *b*) the situation regarding the determination of potentials from phase-shifts (Fröberg *a*, *b*) has materially altered, in that, where there exist discrete states, there exists, instead of a unique potential, a family of potentials for the same phase-shifts, (*b*) although several possible methods for polarising fast neutrons or protons have been suggested [see, for example, Wolfenstein (1949 *a*) and the reference given there], the experimental difficulties in this connection have not yet been overcome.

2. Expressions for $\sigma(\theta\phi)$ and $P(\theta\phi)$

The theoretical expression for the amplitude of the scattered wave, in terms of phase-shifts has been given by Ashkin and Wu (1948) and we shall here directly take their expression. Taking the direction of quantisation for both spin and orbital angular momentum along the incident (z-axis) direction, the asymptotic behaviour of the wave-function at large distances is given by

$$\psi = (A_a \chi_a + \sum_{s=1}^{3} A_s \chi_{m_s}) e^{ikz} + (e^{ikr}/r) \left[A_a S_a \chi_a + \sum_{m_{s'}=-1}^{1} \chi_{m'_s} \sum_{m_s=-1}^{1} S_{s's} A_s \right], \quad (1)$$

in which the subscripts s instead of m_s are sometimes used for simplicity in writing (s taking the values 1, 2 and 3 respectively as m_s takes the values $+1$, -1 and zero), and where the first and the second terms represent the incident and the scattered waves respectively; χ_a is the singlet spin wave

function, χ_{m_s} ($m_s = \pm 1, 0$), are the three triplet spin wave functions, the A's are given in terms of the angles which the spin directions of the two particles in the incident beam make with the direction of quantisation by the identity (3) of (B)* and

$$S_a = \frac{1}{2ik} \sum_{l=0}^{\infty} \left\{ exp\,(2i\delta_l^a) - 1 \right\} P_l^o\,(\cos\theta) \tag{2a}$$

and

$$\mathbf{S}_{s's} = S_{s's} \times exp\,\{i(m_s - m_s')\,\phi\}, \text{ with}$$

$$S_{s's} = \frac{1}{2ik} \sum_{l=0}^{\infty} P_l^{m_s - m_s'}\,(\cos\theta)\,[4\pi\,(2l+1)]^{\frac{1}{2}} \left[\sum_{J=l-1}^{l+1} \{exp\,(2i\delta_l^{Jm_s}) - 1\} \times \right.$$

$$\left. < Slm_s - m_s' m_s' \mid SlJm_s > < SlJm_s \mid Slom_s > \right], \tag{2b}$$

where δ_l^a is the singlet phase-shift corresponding to an orbital angular momentum l (tensor force does not act in singlet states), $\delta_l^{Jm_s}$ is the phase-shift corresponding to an orbital angular momentum l, and a total angular momentum J with its z component m_s and $P_l^{m_s - m'}{}_s\,(\cos\theta)$ are the usual associated Legendre functions. $< Slm_s - m_s'\, m_s' \mid SlJm_s >$ are the well-known matrix elements of a unitary transformation connecting the wave functions in $(SlJJ_z)$ and $(Slm_l\, m_s)$ schemes, and are given in Condon and Shortley (1935). In the equation (2b) the phase-shifts $\delta_l^{Jm_s}$ are to be replaced by zero if the conditions $\mid m_s \mid \leqslant J$, $J \geqslant 0$ and $\mid m_s - m_s' \mid \leqslant l$ are not satisfied. With the explicit forms of $S_{s's}$ given by expressions (23) of Ashkin and Wu (1948) and remembering that

$$\delta_l^{J\,(m_s=1)} = \delta_l^{J\,(m_s=-1)} \text{ and that } P_l^m\,(\cos\theta) = (-1)^m\, P_l^{-m}\,(\cos\theta)$$

it is obvious that the following relations hold between the nine $S_{s's}$

$$S_{11} = S_{22},\ S_{21} = S_{12},\ S_{13} = (-1)\,S_{23} \text{ and } S_{32} = (-1)\,S_{31}. \tag{3}$$

Now as in (B), if the polarisation factor $P\,(\theta\phi)$ is defined as the difference between the absolute probabilities that the spins of the neutrons in the scattered beam point parallel or anti-parallel to the spin direction of the incident neutrons and if we assume the latter to be completely polarised in a direction perpendicular to the incident direction and lying in the $\phi = 0$ plane, then $\sigma\,(\theta\phi)$ and $P\,(\theta\phi)$ are given by putting $\mu = \pi/2$ in equations (4) and (5) of (B). Doing so, we have

$$P\,(\theta\phi) \times \sigma\,(\theta\phi) = p\,(\theta\phi) = \sqrt{2}\ Re\,\{\bar{B}_3\,(B_1 + B_2) + \bar{B}_a\,(B_2 - B_1) \tag{4}$$

* In the left hand side of identity (3) of (B), the two *minus* signs between the terms should read *plus*.

with $$\sigma(\theta\phi) = \bar{B}_a B_a + \sum_{s=1}^{3} \bar{B}_s B_s, \tag{5}$$

in which for brevity, the amplitudes of the scattered waves in the singlet and the three triplet states have been denoted by B_a and B_s ($s = 1, 2$ and 3) respectively and $\bar{B}$ is the complex conjugate of B. Inserting expressions for B's from (1) in (4) and (5) and making use of (2) and (3), we obtain after averaging over all directions of proton spin (since protons are here assumed to be unpolarised)

$$\begin{aligned}\sigma(\theta\phi) &= \tfrac{1}{4}[S_a S_a + S_{33}S_{33} + 2(\bar{S}_{11}S_{11} + \bar{S}_{21}S_{21} + \bar{S}_{31}S_{31} + \bar{S}_{23}S_{23})] \\ &\quad - \frac{1}{\sqrt{2}} \sin\phi \, Re[(i)(\bar{S}_{21}S_{23} + \bar{S}_{31}S_{33} - \bar{S}_{11}S_{23})] \\ &\equiv \sigma_1(\theta) + \sin\phi\sigma_2(\theta), \text{ say} \end{aligned} \tag{6}$$

$$\begin{aligned}\text{and } p(\theta\phi) &= \tfrac{1}{2} Re[\bar{S}_a S_{11} + \bar{S}_{33}S_{11} + \bar{S}_{31}S_{23} + \cos 2\phi(\bar{S}_{33}S_{21} - \bar{S}_a S_{21} \\ &\quad - \bar{S}_{31}S_{23} - \sqrt{2}i \sin\phi(\bar{S}_{31}S_{11} - \bar{S}_{31}S_{21} - \bar{S}_{33}S_{23})] \\ &\equiv p_1(\theta) + \sin\phi \, p_2(\theta) + \cos 2\phi p_3(\theta), \text{ say.} \end{aligned} \tag{7}$$

Expression (6) for $\sigma(\theta\phi)$ is the same as that given by Wolfenstein (1949 *b*) except that here the factor $\sin\phi$ instead of $\cos\phi$ appears, which is understood, because we have taken the direction of polarisation of the incident neutrons along the x-axis ($\phi = 0$ plane) instead of along y-axis as in his Paper.

It may be mentioned here that both $\sigma(\theta\phi)$ and $p(\theta\phi)$ will naturally be independent of ϕ, if the direction of polarisation is taken along the incident direction.

3. Derivation of Equations for the Phase-Shifts

It is seen that both $\sigma(\theta\phi)$ and $p(\theta\phi)$ depend not only on the angle of scattering θ, but also on the azimuth θ of the scattured direction, in contrast to the case for central interaction where they are functions of θ alone. If both $\sigma(\theta\phi)$ and $p(\theta\phi)$ are known from experiments as functions of θ and ϕ, then by multiplying both the left hand side and right-hand side of (6) by 1 and $\sin\phi$, and those of (7) by 1, $\sin\phi$ and $\cos 2\phi$ in turn and integrating over all ϕ we get five equations, namely for $\sigma_1(\theta)$, $\sigma_2(\theta)$, $p_1(\theta)$, $p_2(\theta)$ and $p_3(\theta)$ separately. In these expressions, it is obvious that θ occurs through the products of Legendre or associated Legendre functions $P_l^m(\cos\theta)$ of the type $P_m{}^0 P_n{}^0$, $P_m{}^1 P_n{}^1$, $P_m{}^2 P_n{}^2$, $P_m{}^0 P_n{}^1$ and $P_m{}^1 P_n{}^2$. Each of these products can be expressed as a sum of finite number of either Legendre functions or associated Legendre functions with superscripts (m value) 1 or 2. The expansions needed here are

$$P^0{}_m(\cos\theta)\,P^0{}_n(\cos\theta)=\sum_{r=0}A_{mn,r}\;P^0{}_{m+n-2r}(\cos\theta),\;A_{mn,r}=A_{nm,r}$$

$$P^1{}_m(\cos\theta)\,P^1{}_n(\cos\theta)=\sum_{r=0}B_{mn,r}\;P^0{}_{m+n-2r}(\cos\theta),\;B_{mn,r}=B_{nm,r}$$

$$P^2{}_m(\cos\theta)\,P^2{}_n(\cos\theta)=\sum_{r=0}C_{mn,r}\;P^0{}_{m+n-2r}(\cos\theta),\;C_{mn,r}=C_{nm,r}$$

$$P^0{}_m(\cos\theta)\,P^1{}_n(\cos\theta)=\sum_{r=0}D^{01}{}_{mn,r}\,P^1{}_{m+n-2r}(\cos\theta),\;D^{01}{}_{mn,r}\neq D^{01}{}_{nm,r}$$

$$P^1{}_m(\cos\theta)\,P^2{}_n(\cos\theta)=\sum_{r=0}E^{12}{}_{mn,r}\,P^1{}_{m+n-2r}(\cos\theta),\;E^{12}{}_{mn,r}\neq E^{12}{}_{nm,r}$$

$$P^1{}_m(\cos\theta)\,P^1{}_n(\cos\theta)=\sum_{r=0}F^{11}{}_{mn,r}\,P^2{}_{m+n-2r}(\cos\theta),\;F^{11}{}_{mn,r}=F^{11}{}_{nm,r}$$

$$P^0{}_m(\cos\theta)\,P^2{}_n(\cos\theta)=\sum_{r=0}G^{02}{}_{mn,r}\,P^2{}_{m+n-2r}(\cos\theta),\;G^{02}{}_{mn,r}=G^{02}{}_{nm,r},\qquad(8)$$

in which the summation is for all integral values of r from zero to the lesser of m and n. The coefficients $A_{mn,r}$, $B_{mn,r}$,.... $D_{mn,r}{}^{01}$...., etc. (the superscripts 0, 1 and 2, referring to the m values of the associated Legendre functions in order of the subscripts) can be easily obtained with the help of the integrals of the type $\int_0^\pi P_l^{\mu}(\cos\theta)\,P_m{}^{v}(\cos\theta)\,P_n{}^{w}(\cos\theta)\,\sin\theta\,d\theta$ with $u=v+w$. This integral has been evaluated by Gaunt (1929) and since we shall not need here the actual values of the coefficients in expansions (8), their explicit form will not be given here.

With these expansions it is obvious that $\sigma_1(\theta)$ and $p_1(\theta)$ can be expressed as infinite series in $P_l{}^0(\cos\theta)$ $(l=0, 1, 2....)$, $\sigma_2(\theta)$ and $p_2(\theta)$ as infinite series in $P_l{}^1(\cos\theta)$ $(l=1, 2,....)$, and $p_3(\theta)$ as an infinite series in $P_l{}^2(\cos\theta)$ $(l=2, 3,....)$. Now by using the orthogonal relations

$$\int_0^\pi P_l^m(\cos\theta)\,P_{l'}{}^m(\cos\theta)\sin\theta\,d\theta=\delta_{ll'}\times\frac{2}{2l+1}\frac{(l+m)\,!}{(l-m)\,!},$$

and expressing the numerical values of the integrals

$$\int_0^\pi\sigma_1(\theta)\,P_l{}^0(\cos\theta)\sin\theta\,d\theta,\quad\int_0^\pi\sigma_2(\theta)\,P_l{}^1(\cos\theta)\sin\theta\,d\theta,$$

$$\int_0^\pi p_1(\theta)\,P_l{}^0(\cos\theta)\sin\theta d\theta,$$

$$\int_0^\pi p_2(\theta)\,P_l{}^1(\cos\theta)\sin\theta\,d\theta\text{ and }\int_0^\pi p_3(\theta)\,P_l{}^2(\cos\theta)\sin\theta\,d\theta$$

by α_l, β_l, γ_l, δ_l and π_l respectively, we shall get five sets of infinite number of equations for the unknown scattering parameters (phase-shifts). Writing for simplicity

$$S_{s's} = \sum_{l=0}^{\infty} \lambda^l_{s's} P_l^{m_s - m_{s'}} (\cos\theta) \text{ and } S_a = \sum_{l=0}^{\infty} \lambda_a^l P_l^0 (\cos\theta),$$

the explicit forms for $\lambda_{s's}^{\ l}$ and $\lambda_a^{\ l}$ in terms of phase-shifts being apparent from (2), the five sets of equations are of the form:

$$\alpha_0 = [(\lambda^0{}_a\lambda^0{}_a + 2\bar{\lambda}^0{}_{11}\lambda^0{}_{11} + \bar{\lambda}^0{}_{33}\lambda^0{}_{33})\, A_{00,0} + (\bar{\lambda}^1{}_a\lambda^1{}_a + 2\bar{\lambda}^1{}_{11}\lambda^1{}_{11} + \bar{\lambda}^1{}_{33}\lambda^1{}_{33})\, A_{11,1}$$
$$+ 2\,(\bar{\lambda}^1{}_{31}\lambda^1{}_{31} + \bar{\lambda}^1{}_{23}\lambda^1{}_{23})\, B_{11,1} + \{\lambda^2{}_a\lambda^2{}_a + 2\bar{\lambda}^2{}_{11}\lambda^2{}_{11} + \lambda^2{}_{33}\lambda^2{}_{33})\, A_{22,2}$$
$$+ 2\,(\lambda^2{}_{31}\lambda^2{}_{31} + \bar{\lambda}^2{}_{23}\lambda^2{}_{23})\, B_{22,2} + 2\bar{\lambda}^2{}_{21}\lambda^2{}_{21} \times C_{22,2}\}$$
$$+ \ldots . \textit{terms with higher } l \textit{ (superscripts)}$$

$$\alpha_1 = \tfrac{2}{3}\, Re\,[(\bar{\lambda}^0{}_a\lambda^1{}_a + \ldots .)\, A_{01,0} + (\bar{\lambda}^1{}_a\lambda^2{}_a + \ldots .) A_{12,1} + 2\,(\bar{\lambda}^1{}_{31}\lambda^2{}_{31} + \bar{\lambda}^1{}_{23}\lambda^2{}_{23})\, B_{12,1}$$
$$+ \{(\bar{\lambda}^2{}_a\lambda^3{}_a + \ldots)\, A_{23,2} + 2\,(\bar{\lambda}^2{}_{31}\lambda^3{}_{31} + \bar{\lambda}^2{}_{23}\lambda^3{}_{23})\, B_{23,2} + 2\bar{\lambda}^2{}_{21}\lambda^3{}_{21}\, C_{23,2}\} + t,\, h.\, s.]$$

$$\alpha_2 = \tfrac{1}{5}\,[(\bar{\lambda}^1{}_a\lambda^1{}_a + \ldots .)\, A_{11,0} + 2\,(\bar{\lambda}^1{}_{31}\lambda^1{}_{31} + \bar{\lambda}^1{}_{23}\lambda^1{}_{23})\, B_{11,0} + \{(\lambda^2{}_a\lambda^2{}_a + \ldots .)\, A_{22,1}$$
$$+ 2\,(\bar{\lambda}^2{}_{31}\lambda^2{}_{31} + \bar{\lambda}^2{}_{23}\lambda^2{}_{23})\, B_{22,1} + 2\bar{\lambda}^2{}_{21}\lambda^2{}_{21} \times C_{22,1}\} + \ldots .\ t.\ h.\ s.$$
$$+ (\bar{\lambda}^0{}_a\lambda^2{}_a + \ldots . + \textit{complex conjugate})\, A_{02,0} + (\lambda^1{}_a\lambda^3{}_a + \ldots . + c.c.)\, A_{13,1}$$
$$+ 2\,(\bar{\lambda}^1{}_{31}\lambda^3{}_{31} + \bar{\lambda}^1{}_{23}\lambda^1{}_{23})\, B_{13,1} + \ldots .\ t.h.s.]$$
$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$\beta_1 = -\frac{4}{3\sqrt{2}}\, Im\,[(\bar{\lambda}^1{}_{31}\lambda^0{}_{33} - \bar{\lambda}^1{}_{23}\lambda^0{}_{11})\, D^{10}{}_{10,0} + (\bar{\lambda}^1{}_{31}\lambda^2{}_{33} - \bar{\lambda}^1{}_{23}\lambda^2{}_{11})\, D^{10}{}_{12,1}$$
$$+ (\bar{\lambda}^2{}_{31}\lambda^1{}_{33} - \bar{\lambda}^2{}_{23}\lambda^1{}_{11})\, D^{10}{}_{21,1} + \lambda^1{}_{23}\lambda^2{}_{21}\, E^{12}{}_{12,1} + \ldots .\ t.h.s.]$$

$$\beta_2 = -\frac{12}{5\sqrt{2}}\, Im\,[2\,(\bar{\lambda}^1{}_{31}\lambda^1{}_{33} - \bar{\lambda}^1{}_{23}\lambda^1{}_{22})\, D^{10}{}_{11,0} + (\bar{\lambda}^2{}_{31}\lambda^2{}_{33} - \bar{\lambda}^2{}_{23}\lambda^2{}_{11})\, D^{10}{}_{22,1}$$
$$+ 2\bar{\lambda}^2{}_{21}\lambda^2{}_{21}\, E^{12}{}_{22,1} + \ldots .\ t.h.s.$$
$$+ (\lambda^2{}_{31}\lambda^0{}_{33} - \lambda^2{}_{23}\lambda^0{}_{11})\, D^{10}{}_{20,0} + (\lambda^1{}_{31}\lambda^3{}_{33} - \bar{\lambda}^1{}_{23}\lambda^3{}_{11})\, D^{10}{}_{13,1}$$
$$+ (\lambda^3{}_{31}\lambda^3{}_{33} - \lambda^3{}_{23}\lambda^1{}_{11})\, D^{10}{}_{31,1} + \bar{\lambda}^1{}_{23}\lambda^3{}_{21} \times E^{12}{}_{13,1} + \ldots .\ t.h.s.]$$
$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$\gamma_0 = Re\,[(\lambda^0{}_a + \bar{\lambda}^0{}_{33})\, \lambda^0{}_{11}\, A_{00,0} + (\lambda^1{}_a + \bar{\lambda}^1{}_{33})\, \lambda^1{}_{11} A_{11,1} + \lambda^1{}_{31}\lambda^1{}_{23}\, B_{11,1} + \ldots .\ t.h.s.]$$

$$\gamma_1 = \tfrac{1}{3}\, Re\,[(\bar{\lambda}^0{}_a + \bar{\lambda}^0{}_{33})\, \lambda^1{}_{11} A_{01,0} + (\bar{\lambda}^1{}_a + \bar{\lambda}^1{}_{33})\, \lambda^0{}_{11}\, A_{10,0} + (\bar{\lambda}^1{}_a + \bar{\lambda}^1{}_{33})\, \lambda^2{}_{11} A_{12,1}$$
$$+ (\bar{\lambda}^2{}_a + \bar{\lambda}^2{}_{33})\, \lambda^1{}_{11} A_{21,1} + \bar{\lambda}^1{}_{31}\lambda^2{}_{23}\, B_{12,0} + \bar{\lambda}^2{}_{31}\lambda^1{}_{23} B_{21,0} + \ldots .\ t.h.s.]$$

$$\gamma_2 = \tfrac{1}{5}\, Re\,[(\bar{\lambda}^1{}_a + \bar{\lambda}^1{}_{33})\,\lambda^1{}_{11}A_{11,0} + \bar{\lambda}^1{}_{31}\lambda^1{}_{23}\,B_{11,0} + \ldots . t.h.s.$$
$$+ \{(\bar{\lambda}^0{}_a + \bar{\lambda}^0{}_{33})\,\lambda^2{}_{11}A_{02,0} + (\bar{\lambda}^2{}_a + \bar{\lambda}^2{}_{33})\,\lambda^0{}_{11}A_{20,0} + (\bar{\lambda}^1{}_a + \bar{\lambda}^1{}_{33})\,\lambda^3{}_{11}A_{13,1}$$
$$+ (\bar{\lambda}^3{}_a + \bar{\lambda}^3{}_{33})\,\lambda^1{}_{11}A_{31,1} + (\bar{\lambda}^1{}_{31}\lambda^3{}_{23} + \bar{\lambda}^3{}_{31}\lambda^1{}_{23})\,B_{13,1}\} + \ldots . t.h.s.]$$

.....

$\delta_1 =$ } Replace everywhere in β_1 and β_2 respectively, λ_{31} by λ_{23} and
$\delta_2 =$ } *vice-versa.*

.....

$$\pi_2 = \frac{24}{5}\, Re\,[-\lambda^1{}_{31}\lambda^1{}_{23}F_{11.0} - \lambda^2{}_{31}\lambda^2{}_{23}F_{22,1} + (\bar{\lambda}^2{}_{33} - \bar{\lambda}^2{}_a)\,\lambda^2{}_{21}G^{02}{}_{22,1} + \ldots . t.h.s.$$
$$+ (\bar{\lambda}^0{}_{33} - \lambda^0{}_a)\,\lambda^2{}_{21}G^{02}{}_{02,0} - (\bar{\lambda}^1{}_{31}\lambda^3{}_{23} + \lambda^3{}_{31}\lambda^1{}_{23})\,F_{13,1} + (\bar{\lambda}^1{}_{33} - \bar{\lambda}^1{}_a)\,\lambda^3{}_{21}G^{02}{}_{13,1}$$
$$+ \ldots . t.h.s.$$

.....

4. Solution for the Phase-Shifts

One can solve these equations for the phase-shifts, by successive approximations, to any desired accuracy, by a procedure similar to that adopted in (B) for the case where interaction was wholly central. We first assume that all the phase-shifts corresponding to orbital angular momentum l are $\gg$ all the phase-shifts corresponding to orbital angular momentum $(l+1)$ and so on and that unity is $\gg$ all the phase-shifts corresponding to orbital angular momentum zero; under these assumptions the largest term in any $(\alpha = \ldots . \beta = \ldots ., \text{etc.})_l$ is a small quantity of the order $(l+1)$, the rest being higher order quantities. Then as in (B) one would expect to determine all phase-shifts for the partial wave of orbital angular momentum l, in the first approximation by the equations $(\alpha = \ldots ., \beta = \ldots ., \text{etc.})_l$ by retaining in them terms of the lowest order, provided all phase-shifts for lower l have been determined in the first approximation by the previous equations. Then by retaining in the equations for any l, higher order terms as well, and substituting the first order phase-shifts, one could determine the phase-shifts to a second approximation.

This procedure needs a slight modification in this case, as will be clear from the following. In Table I below, we give the number of equations available for any l up to $l=4$ and the number of phase-shifts to be determined:

TABLE I

l	Equations	Real Phase-shifts	Complex Phase-shifts	l	Equations	Real Phase-shifts	Complex Phase-shifts
0	$\alpha_0 =$ $\gamma_0 =$	$\delta_0{}^a$	$\delta_0{}^{1,1}$, $\delta_0{}^{1,0}$	III	$\alpha_3 =$ $\beta_3 =$ $\gamma_3 =$ $\delta_3 =$ $\pi_3 =$	$\delta_3{}^a$ $\delta_3{}^{3,1}$	$\delta_3{}^{2,1}$, $\delta_3{}^{2,0}$ $\delta_3{}^{4,1}$, $\delta_3{}^{4,0}$
I	$\alpha_1 =$ $\beta_1 =$ $\gamma_1 =$ $\delta_1 =$	$\delta_1{}^a$, $\delta_1{}^{1,1}$ $\delta_1{}^{0,0}$	$\delta_1{}^{3,1}$, $\delta_1{}^{2,0}$				
II	$\alpha_2 =$ $\beta_2 =$ $\gamma_2 =$ $\delta_2 =$ $\pi_2 =$	$\delta_2{}^a$, $\delta_2{}^{2,1}$	$\delta_2{}^{1,1}$, $\delta_2{}^{1,0}$ $\delta_2{}^{3,1}$, $\delta_2{}^{3,0}$	IV	$\alpha_4 =$ $\beta_4 =$ $\gamma_4 =$ $\delta_4 =$ $\pi_4 =$	$\delta_4{}^a$ $\delta_4{}^{4,1}$	$\delta_4{}^{3,1}$, $\delta_4{}^{3,0}$ $\delta_4{}^{5,1}$, $\delta_4{}^{5,0}$

Since $\delta_0{}^{1,1}$ and $\delta_0{}^{1,0}$ are complex phase-shifts it appears that there are five unknown constants for S sphase-shifts and only two equations; similarly say for order l, since there are four phase-shifts which are complex, there will appear to be ten unknown constants. However, actually, as is well known, the four complex phase-shifts of the type $\delta^{l,1}{}_{l-1}$, $\delta^{l,0}{}_{l-1}$ and $\delta^{l,1}{}_{l+1}$, $\delta^{l,0}{}_{l+1}$ in themselves only involve three unknown real constants [see for example, Ashkin and Wu (1948)]. This fact makes the determination of the unknown parameters and thus of the phase-shifts possible. One proceeds as follows:

(1) Assume first $\delta_0{}^{1,1}$ and $\delta_0{}^{1,0} = \delta_0$ say, to be real and equal—this would be actually so, if the tensor force was zero—then $\delta_0{}^a$ and δ_0 can be determined in the first approximation from the two ($l = 0$) equations. In fact, these two equations reduce to the equations (14) of (B) and give in all, four possible pairs of solutions for $\delta_0{}^a$, δ_0. Assuming any one pair of solutions to be the correct one—to choose the correct pair one has to make use of other properties of the neutron proton system [*cf.*, (B), p. 507]—one could then proceed to determine other phase-shifts as follows:—

(2) Assume $\delta_1{}^{2,1} = \delta_1{}^{2,0} =$ real; substituting the values for $\delta_0{}^a$ and δ_0 derived from step (1) deduce $\delta_1{}^a$, $\delta_1{}^{1,1}$, $\delta_1{}^{0,0}$ and $\delta_1{}^{2,1} = \delta_1{}^{2,0}$ (real) from ($l =$ I) equations (see Table I) which are of the first degree in the unknowns (taking lowest order terms only in these equations).

(3) Assume $\delta_2{}^{3,1} = \delta_2{}^{3,0} =$ real; combine equations ($l = 0$ and II) up to third order in δ's, substituting δ_1's from step (2), then the number of

equations is seven and the number of unknown constants (various δ_2's and δ_0's) is also 7. Hence one gets at this stage both the real and imaginary parts of all the four complex phase-shifts for $J=1$ state, namely, $\delta_0^{1,1}$, $\delta_0^{1,0}$, $\delta_2^{1,1}$ and $\delta_2^{1,0}$.

(4) Assume $\delta_3^{4,1}=\delta_3^{4,0}=$ real; combine equations (III and I) up to fourth order in δ's substituting for δ_0's, δ_2's, etc., as derived from step (3), then the number of equations is nine and the number of unknowns is also nine.

(5) Assume $\delta_4^{5,1}=\delta_4^{5,0}=$ real. Combine any one of the equations II up to fifth order with IV, substituting in these equations from step (3) all values for δ's, except for $\delta_2^{3,1}$ and $\delta_2^{3,0}$ which now together with $\delta_4^{3,1}$ and $\delta_4^{3,0}$ comprise three unknown constants; with this the number of unknown constants becomes 6 and so is the number of equations.

In this way we can proceed step by step to determine all the unknowns in the first approximation.

Phase-shifts to higher approximations can be determined by substituting the values for δ's obtained in the first approximation in suitable equations; *e.g.*, for phase-shifts in step (3) one can now substitute instead of $\delta_2^{3,1}=\delta_2^{3,0}$, the phase-shifts as determined by step (5) and also values of phase-shifts determined by step (4).

Summary

The study of scattering and the consequent depolarisation of a polarised beam of neutrons on being scattered by an unpolarised proton gas has been suggested earlier by Bhatia (1949, 1950) as a means of obtaining information about *N–P* interaction. In this note a general expression for the polarisation factor for the scattered neutrons has been derived in terms of phase-shifts, when the *N–P* interaction has a non-central term as well. Further it is shown that from a knowledge of the scattering and the polarisation cross-sections as functions of θ and ϕ (the angle and the azimuth of scattering), it is possible to obtain all the unknown phase-shifts, which determine the scattering. This is of interest, since knowledge of the phase-shifts as functions of the energy of the particles, enables one to determine the interaction potentials themselves, at least in the first approximation.

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NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

Part XXXII. Some Coumarin Derivatives

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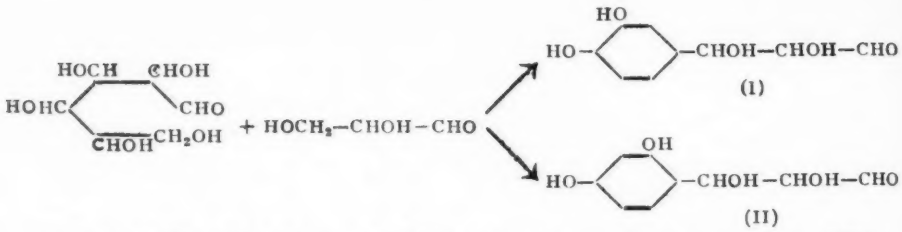
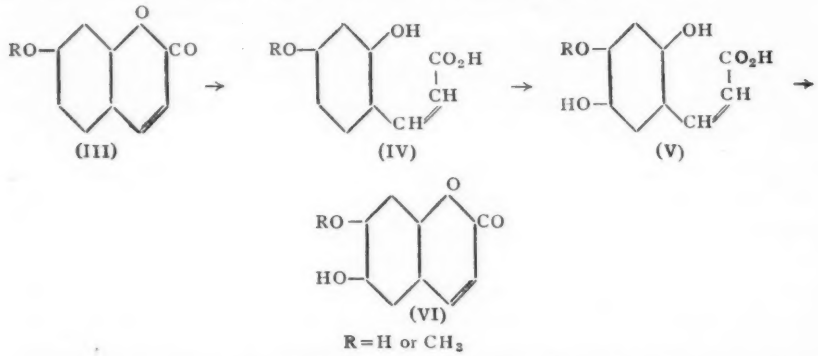
The C_6-C_3 unit is not only present as a component of anthoxanthin and anthocyanin molecules, but it also exists in the form of a large number of simpler compounds. The C_3 side chain takes every possible form, amino acid in phenyl alanine derivatives, allyl and propenyl chains in components of essential oils, and other unsaturated forms in cinnamic acids, aldehydes and alcohols; phenyl propane derivatives are present in lignins. The lignane group of compounds represent combinations of two C_6-C_3 units. In all these there is a general resemblance in the nature and location of the substituents, hydroxyl and methoxyl groups in the benzene ring. According to Robinson[1] the catechol (3:4-dihydroxy phenyl) form (I) is the most fundamental and the others are derived from it by stages involving oxidation or reduction. As far as oxidation is concerned the validity of this suggestion has been supported by laboratory experiments with flavonols and allyl and propenyl benzene derivatives.[2]

There are however cases of anthoxanthins having the hydroxyl groups of the side phenyl nucleus in the 2′ and 4′ positions, *e.g.*, morin, cyanomaclurin, pterocarpin and homopterocarpin. Even rotenone may be considered to be derived from such a side phenyl nucleus. It was therefore suggested in one of our earlier publications[3] that as a less common alternative the resorcinol derivative (II) is also produced by the condensation of a hexose and triose and this undergoes changes in the same way as the catechol derivative. If the side chain gets transformed into a cinnamic acid, a coumarin will result. On this basis umbelliferone will represent the simplest member of the group and the others should be derived from it by processes involving oxidation and reduction. This idea appears to fit in with the common occurrence of 6:7 and 7:8-dihydroxy substituted compounds in coumarins, types which are not met with in the anthocyanin and anthoxanthin series. It is therefore developed here using laboratory experiments in support.

Bargellini[4] showed that umbelliferone methyl ether (III, $R = CH_3$) can be oxidised by means of alkaline persulphate to yield 7-methoxy-6-hydroxy



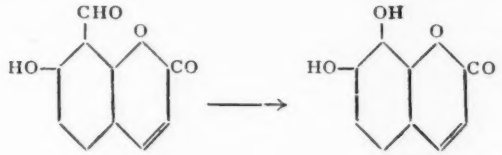
coumarin (VI). He did not give the yield; in our experiments about 20% yield is obtained. Obviously the reaction involves the formation of a coumarinic acid (IV) and its oxidation in the position *para* to the liberated hydroxyl group. In nature a stabler form in which the pyrone ring is open should be involved in this *para* oxidation. Consequently experiments have now been carried out employing the corresponding coumaric acid (umbellic acid methyl ether) for oxidation. The yield (about 25%) is not appreciably different. Umbelliferone (III, R = H) itself could be directly oxidised by this method to yield æsculetin (VI, R = H). Though the yield is rather low, this method is handy for getting free æsculetin readily.



Parallel series of experiments have now been carried out with 4-methyl umbelliferone and its methyl ether with ver similar results. That geometrical inversion takes place more readily in 4-methyl substituted coumarins has been pointed out earlier by Murti, Rao and Seshadri[5] and this knowledge has been used in our experiments. It may be mentioned here that 4-methyl æsculetin was subjected to partial methylation by Bargellini and Martegiani[6] who considered that the resulting monomethyl ether having m.p. 173–75° might be either the 7 or 6-monomethyl ether. No derivatives were described. The above authors used methyl iodide and methyl alcoholic potash at 100°. More recently Velluz and Amiard[7] have employed for this

partial methylation, dimethyl sulphate and aqueous sodium carbonate solution. They consider the product to be the 7-monomethyl ether and report its melting point as 208–9°, the acetate melting at 200–01°. We have been able to repeat their experiments and confirm their results. The product of oxidation of 4-methyl-7-methoxy coumarin melts also at 208–9° and yields an acetate melting at 199–200°; the mixed melting points were undepressed. Since on further methylation both yield 4-methyl æsculetin-dimethyl ether there is no doubt that they are correctly represented as 4-methyl-æsculetin-7-methyl ether.

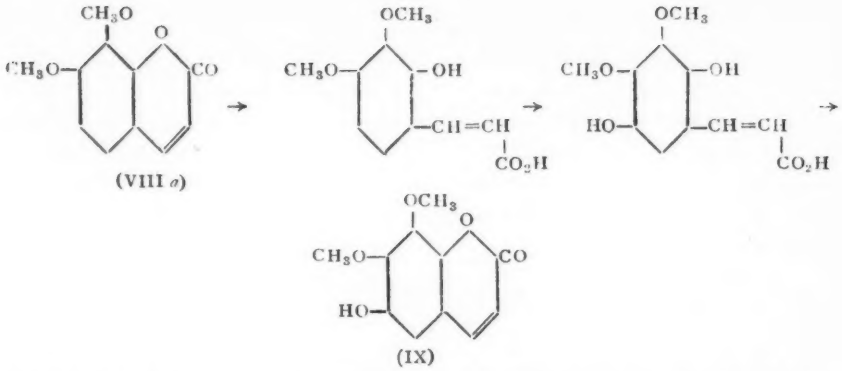
No experiment seems to have been made in the past to get daphnetin from umbelliferone. This has now been accomplished by adopting the two stage process of *ortho* nuclear oxidation. Umbelliferone condenses with hexamine to yield the 8-aldehyde (VII)[8] which undergoes smooth oxidation with alkaline hydrogen peroxide to give high yields of daphnetin (VIII). Similarly from 4-methyl-umbelliferone-8-aldehyde, 4-methyl daphnetin is made. These experiments suggest the possible biogenesis of æsculetin, daphnetin and their derivatives from umbelliferone by *para-* and *ortho-*oxidation respectively.



(VII) (VIII)

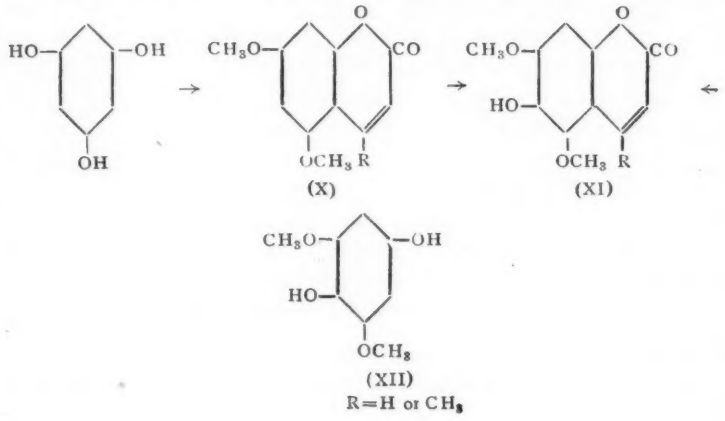
As compared with the anthocyanins and anthoxanthins, compounds containing the 6:7:8 arrangement of hydroxyl and methoxyl groups are markedly common in the coumarin group and are represented by fraxetin, fraxidin and isofraxidin. There are two ways in which they could be derived (i) *ortho* oxidation of æsculetin and its derivatives and (ii) *para* oxidation of daphnetin and its derivatives. Process (i) using scopoletin should be feasible and it is being studied. On the other hand, process (ii) using daphnetin dimethyl ether (VIII *a*) has already been examined by Bargellini.[9] He has recorded a yield of 10% of (IX). In our experiments using direct oxidation the yield was 15%, and introducing conversion to coumaric acid as an intermediate stage the yield was about 30%. On methylation it yields fraxetin dimethyl ether. The dimethyl ether of 4-methyl daphnetin gives similar yields of the oxidation product, 4-methyl-7:8-dimethoxy-6-hydroxy coumarin.

It should however be mentioned here that limettin (X, R = H) (5:7-dimethoxy coumarin) and derived compounds do not fall into line with the



(VIII *a*) (IX)

above scheme since no direct method of obtaining them from umbelliferone is known. They should therefore indicate the existence of an alternative process of evolution based on phloroglucinol and triose units. In laboratory synthesis they are obtained starting from phloroglucinol. On this basis fraxinol (XI, R = H) could be considered to be directly obtained from limettin by *para* oxidation in the 6-position. Though it is possible to obtain 5:6:7-trihydroxy (methoxy) coumarins from 6:7-dihydroxy compounds by partial methylation in the 7-position and *ortho*-oxidation in the 5-position, the structure of fraxinol with a free hydroxyl in the 6-position would support its biogenetic relationship with limettin. Experiments carried out on the direct *p*-oxidation of 4-methyl-limettin (X, R= CH_3) in alkaline solution gave only poor yields of the oxidation product. But when preliminary conversion is effected to produce the coumaric acid (4-methyl limettic acid) and then oxidation carried out, fair yields (20%) of 4-methyl fraxinol (XI,

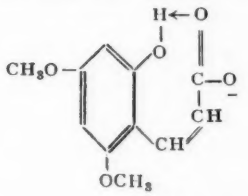


(X) (XI)

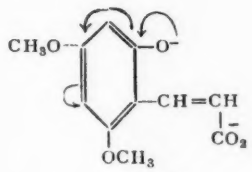
(XII)
R=H or CH_3

R = CH_3) are obtained. It is most convenient to carry out the conversion, oxidation of the coumaric acid and final reconversion into coumarin all in one continuous operation. For purposes of comparison 4-methyl-fraxinol is now also synthesised using 2:6-dimethoxy-quinol (XII) and acetoacetic ester.

The yield of the pure products in the persulphate oxidation is generally poor in the coumarin series though in some cases the crude yields may be high. This seems to be partly due to the formation of coloured by-products. The difference in the behaviour of the *cis* and *trans* acids is marked in the case of disubstituted coumarins particularly when the 5- and 7-positions are occupied. A possible explanation of this observation may be the existence of hydrogen bond in the *cis* form (XIII) which will reduce the ionisation of the phenolic hydroxyl and the development of strong anionoid (nucleophilic) activity in the required *para* position.



(XIII)



(XIV)

Experimental

Para- *oxidation of umbelliferone and 4-methyl umbelliferone*

To a stirred solution of umbelliferone (5 g.) in aqueous sodium hydroxide (4 g. in 100 c.c.), cooled in ice-water, was added dropwise with stirring a solution of sodium persulphate (7·2 g.) in water (100 c.c.) in the course of two hours. After twenty-four hours, the solution was just acidified with hydrochloric acid (congo red) when unchanged umbelliferone (1·5 g.) was precipitated. It was filtered and the filtrate extracted twice with ether to remove any traces of umbelliferone remaining in solution. Concentrated hydrochloric acid (60 c.c.) and sodium bisulphite (1 g.) were then added to the aqueous solution which was heated in a boiling water-bath for half an hour. On cooling the solution æsculetin was obtained as a dark brown precipitate. It was filtered and purified by repeated crystallisations from aqueous alcohol when it was obtained as pale yellow needles melting at 267–8°. It was soluble in aqueous sodium hydroxide and sodium carbonate and gave a grass green colour with alcoholic ferric chloride. Mixed melting point with an authentic sample of æsculetin was not depressed. Its diacetate

was prepared by refluxing with acetic anhydride and a drop of pyridine. It crystallised from ethyl acetate as colourless needles melting at 135–6°.

Under the same conditions 4-methyl umbelliferone yielded 4-methyl æsculetin crystallising from alcohol as clusters of pale yellow prisms melting at 269–70°. It was identical with a sample prepared by the method of Pechmann and Krafft.[10] The diacetate crystallised from ethyl acetate in the form of colourless needles and melted at 134–5°.

The yield of the pure oxidation product in both cases was about 10%. Changing the conditions such as working up soon after the completion of the addition of persulphate and using a lower temperature for hydrolysing the sulphate did not improve the yield.

p-*Oxidation of 7-methoxy coumarin*

This was originally carried out by Bargellini and Monti[4] with alkaline potassium persulphate in the presence of ferrous sulphate. The yield was not reported. Omitting ferrous sulphate we were able to obtain a yield of 20%. Experiments were made preparing the corresponding coumaric acid, subjecting it to oxidation with alkaline persulphate and converting the product into the coumarin. Eventually a continuous process was adopted as follows:

The methoxy coumarin was converted into the corresponding coumaric acid (4-*O*-methyl-umbellic acid) by treatment with aqueous alkali and mercuric oxide according to the method of Rao and Seshadri.[14] Mercuric oxide was filtered off and the alkaline solution treated with potassium persulphate. After the completion of the addition (with or without allowing to stand overnight) the solution was rendered just acid and extracted with ether to remove the unoxidised material. Then it was acidified strongly after adding some sodium bisulphite and heated to hydrolyse the sulphate ester. The product was extracted with ether repeatedly and the ether extract evaporated. The residue was treated with a small amount of alcohol and mercuric chloride (0·1 g. for 1 g. of the coumaric acid) and heated at 100° for 2 hours. Towards the end strong hydrochloric acid (1 c.c.) was added and the mixture allowed to cool. The final product came out as a solid, but it was extracted with ether and the ether solution evaporated; the residue crystallised from alcohol or ethyl acetate as colourless rectangular prisms melting at 184–5°. The yield was about 25%.

p-*Oxidation of* 4-*methyl*-7-*methoxy coumarin to* 4-*methyl*-7-*methoxy*-6-*hydroxy-coumarin*

4-Methyl-7-methoxy coumarin (5 g.) was dissolved in hot sodium hydroxide (100 c.c., 10%), cooled in ice-water and oxidised with potassium per-

sulphate (11·5 g.). The product crystallised from ethyl acetate as colourless elongated rectangular prisms melting at 208–9°. Yield 1·2 g. (Found: C, 63·8, H, 4·9; $C_{11}H_{10}O_4$ requires C, 64·0, H, 4·9%).

The acetate was prepared by refluxing it with acetic anhydride and a drop of pyridine. It could be crystallised from ethyl acetate as colourless shining rectangular prisms melting at 199–200° (Found: C, 63·4, H, 5·1; $C_{13}H_{12}O_5$ requires C, 62·9, H, 4·8%).

Methylation was effected by means of dimethyl sulphate and potassium carbonate in dry acetone solution. The product crystallised from ethyl acetate as colourless rectangular prisms melting at 143–44°. The mixed melting point with an authentic sample of 4-methyl æsculetin dimethyl ether was undepressed.

4-Methoxy-β-methyl coumaric acid[5] produced from 7-methoxy-4-methyl-coumarin (5 g.) was oxidised with alkaline sodium persulphate in the same way as in a previous experiment. After hydrolysis, the oxidation product was directly converted into the coumarin without being isolated. 7-Methoxy-6-hydroxy-4-methyl coumarin thus obtained (1·7 g.) crystallised from ethyl acetate in the form of elongated rectangular prisms melting at 208–9°, agreeing in every respect with the product obtained directly from 4-methyl-7-methoxy coumarin. Mixed melting point with the product of partial methylation of 4-methyl-æsculetin was undepressed.

Dakin's oxidation of umbelliferone-8-aldehyde

Umbelliferone-8-aldehyde[8] (1 g.) was dissolved in pyridine (5 c.c.) and the solution was added to aqueous sodium hydroxide (0·3 g. in 25 c.c. of water) with cooling. The mixed solution was treated with hydrogen peroxide (6 c.c., 6%) dropwise and with cooling when the temperature appreciably exceeded the room temperature. After addition it was left aside for 2 hours, then acidified, saturated with sodium chloride and extracted with ether 4 times. The ether solution was washed successively with dilute hydrochloric acid and water. On distilling the ether, daphnetin was left behind as a crystalline solid. It crystallised from ethyl acetate in the form of pale yellow rectangular prisms melting at 257-8°. It gave a grass green colour with alcoholic ferric chloride. Yield 0·6 g. Mixed melting point with an authentic sample of daphnetin prepared from pyrogallol and malic acid was undepressed. The dimethyl ether crystallised from boiling water to give colourless needles melting at 119–20°. Mixed melting point with an authentic sample of daphnetin dimethyl ether was undepressed.

Dakin's oxidation of 4-methyl umbelliferone-8-aldehyde

The oxidation was carried out in the same way as in the case of umbelliferone-8-aldehyde. 4-Methyl daphnetin thus obtained crystallised from alcohol in the form of pale yellow rectangular prisms melting at 235–6°. Mixed melting point with a sample prepared according to the method of Pechmann and Duisberg[11] was undepressed. Yield 0·8 g. of 4-methyl daphnetin from 1 g. of 4-methyl umbelliferone-8-aldehyde.

The dimethyl ether crystallised from ethyl acetate as colourless rectangular plates melting at 132–3°. Mixed melting point with an authentic sample was undepressed.

Methylenation

This was carried out by refluxing 4-methyl daphnetin (5 g.) in acetone solution (500 c.c.) with methylene iodide (10·5 g., 1·5 moles) and anhydrous potassium carbonate (10 g.) for 16 hours. The solution was then filtered and the potassium salts washed with hot acetone. The combined filtrate and washings was then distilled to remove the solvent; the residue crystallised from alcohol as pale yellow plates melting at 226–27°. (Yield 1 g., about 20%). Earlier Baker and Savage[12] carried out this methylenation using aqueous alkali, acetone and methylene sulphate and the yield was 8%.

p-*Oxidation of 4-methyl-daphnetin-dimethyl ether*

(i) The dimethyl ether (5 g.) was dissolved in aqueous sodium hydroxide (100 c.c., 10%) by warming and also adding a few drops of pyridine. A saturated solution of potassium persulphate (12 g.) was added drop by drop and with constant stirring, to the above solution cooled in ice-water. After 24 hours, the product was worked up as usual. 6-Hydroxy-7: 8-dimethoxy-4-methyl coumarin crystallised from ethyl acetate to give colourless tiny prisms melting at 173–4°. Some more of it could be obtained by extracting the filtrate with ether. Total yield 0·8 g.

(ii) 7: 8-Dimethoxy-4-methyl coumarin (5 g.) was dissolved in hot aqueous potassium hydroxide (100 c.c., 10%). The solution was cooled, yellow mercuric oxide (2 g.) added and the mixture stirred for 2 hours. The solution was maintained below 10° C. The mercuric oxide was then filtered off and more aqueous potassium hydroxide (25 c.c., 10%) was added. Potassium persulphate (12 g.) was then added under conditions described in previous experiments. After 24 hours, the solution was saturated with hydrogen sulphide, acidified with hydrochloric acid and the dark brown precipitate filtered. The filtrate was extracted with ether.

The sulphate present in the aqueous solution was then hydrolysed with concentrated hydrochloric acid (40 c.c.) at 80° for thirty minutes. The mixture was cooled and shaken with mercuric chloride (0·5 g.). The solid that separated was filtered. Some more of it was obtained when the filtrate was saturated with sodium chloride, extracted with ether and the ether solution evaporated. Total yield 1·5 g. 7: 8-Dimethoxy-6-hydroxy-4-methyl coumarin thus obtained was crystallised from ethyl acetate to give colourless tiny prisms melting at 173–4° (Found: C, 61·1, H, 5·1; $C_{12}H_{12}O_5$ requires C, 61·0, H, 5·1%).

The above product (0·5 g.) was methylated by refluxing in acetone solution (50 c.c.) with dimethyl sulphate (0·5 g.) and potassium carbonate (5 g.) for 6 hours. It was filtered and the filtrate distilled to remove the solvent. The trimethyl ether crystallised from ethyl acetate to give colourless thin rectangular prisms melting at 108–9° (Found: C, 62·1, H, 5·6; $C_{13}H_{14}O_5$ requires C, 62·4, H, 5·6%).

p-*Oxidation of daphnetin-dimethyl ether*

Daphnetin dimethyl ether (2 g.) was dissolved in aqueous potassium hydroxide (50 c.c., 10%) and was stirred with yellow mercuric oxide (1 g.) for two hours. It was filtered, the coumaric acid solution oxidised with potassium persulphate (5 g.) and the product worked up as described for the oxidation of umbelliferone-methyl-ether. 7: 8-Dimethoxy-6-hydroxy coumarin came out as colourless rectangular plates melting at 184–85°; yield 0·6 g. Bargellini[9] reported a melting point of 184° for this compound.

4-*Methyl fraxinol*

(i) *Direct oxidation of 4-methyl limettin.*—4-Methyl limettin (5 g.) was dissolved in aqueous sodium hydroxide (100 c.c., 10%) by warming and also adding a few drops of pyridine. A saturated solution of potassium persulphate (12 g.) was added to the above solution, cooled in ice-water, drop by drop and with constant stirring. After 24 hours the product was worked up as usual. It crystallised from ethyl acetate to give colourless stout prisms melting at 193–4°. Yield 5% (Found: C, 61·3, H, 5·4; $C_{12}H_{12}O_5$ requires, C, 61·0, H, 5·1%).

(ii) *Oxidation through coumaric acid.*—5: 7-Dimethoxy-4-methyl coumarin (5 g.) was dissolved in hot aqueous potassium hydroxide (100 c.c., 10%). The solution was cooled, yellow mercuric oxide (2 g.) added and the mixture stirred for two hours. The solution was maintained below 10°. The mercuric oxide was then filtered off and more aqueous potassium hydroxide

(25 c.c., 10%) was added. Potassium persulphate (12 g.) was then added slowly and the product worked up as described under 4-methyl daphnetin. 4-Methyl fraxinol thus obtained crystallised from ethyl acetate to give colourless stout prisms melting at 193–4°, identical with the sample described above; yield 20%.

Methylation was carried out by refluxing 4-methyl fraxinol (0·5 g.) in acetone solution (50 c.c.) with dimethyl sulphate (0·5 g.) and potassium carbonate (5 g.) for 6 hours. The mixture was filtered and the filtrate distilled to remove the solvent. The methyl ether of 4-methyl fraxinol crystallised from ethyl acetate as colourless thick rhombic plates melting at 113–14°.

The acetate crystallised from ethyl acetate as colourless broad rectangular plates melting at 167–8°.

(iii) *Synthesis.*—2: 6-Dimethoxy quinol was prepared by the method of Spath and Jerzmanowska-Sienkiewiczowa.[18] 2: 6-Dimethoxy quinol (2 g.) was made into a thin paste with ethyl acetoacetate (1·5 g.) and slowly added to concentrated sulphuric acid (5 c.c.) cooled in ice and stirred well. It was left in the refrigerator overnight, and then poured into 50 c.c. of ice-water. The precipitated solid was filtered after keeping for 2 hours, washed with a little water and dried. It crystallised from dry ethyl acetate in the form of colourless stout prisms melting at 193–4°. It agreed in every respect with the nuclear oxidation product of 4-methyl limettin and the mixed melting point was undepressed. The methyl ether of the synthetic product melted also at 113–14° and the acetate at 167–68° and these were identical with the methyl ether and acetate of the nuclear oxidation product.

Summary

It is suggested that umbelliferone is a fundamental compound in the biogenesis of coumarins and that other important hydroxycoumarins involve further stages of oxidation. In support of this idea experiments are described for the preparation from umbelliferone of æsculetin by *p*-oxidation and daphnetin by *ortho*-oxidation. From either of these dihydroxycoumarins, 6: 7: 8-trihydroxycoumarin can be prepared. Limettin would, however, appear to have a different origin. The possible evolution of fraxinol from limettin by *p*-oxidation is supported by persulphate oxidation experiments using 4-methyl limettin. 4-Methyl fraxinol has also been synthesised from 2: 6-dimethoxyquinol and acetoacetic ester.

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FURTHER STUDIES ON THE TEMPERATURE VARIATION OF THE REFRACTIVE INDEX OF CRYSTALS

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1. Introduction

The temperature coefficient of refraction dn/dt of a number of crystals has been measured by Reed (1898) over a range of wavelengths in the visible region from room temperature to 500° C. and by Micheli (1902) from λ 2000 to λ 6000 at a single temperature of 60° C. No high temperature measurements are available in the ultra-violet. The present paper describes interferometric measurements of dn/dt in the ultra-violet and visible regions from room temperature to 400° C. for a number of crystals, namely lithium fluoride, fluorspar, magnesia, quartz and barite. For some of these crystals, additional measurements have been made for the λ 4047, λ 4916 and λ 5790 radiations of mercury at 50° C. The values presented in this paper for the visible region are more accurate than the earlier measurements of the author for some of these crystals. Using these accurate data and the dispersion formulæ for these substances, some of them freshly computed by the author, the rate of shift of the ultra-violet frequencies with temperature is evaluated. This rate is invariably found to increase with temperature.

2. The Method of Measurement

The method of measuring dn/dt in the ultra-violet was a modification of the techniques used earlier for visual studies (Radhakrishnan, 1947 *b*; 1950 *a*, *b*). The wavelengths used were the radiations of the mercury arc at λ 3650 and λ 2537. The former was obtained from a point-source quartz mercury arc, and monochromatized by passing through a Corning glass filter. (A faint trace of the λ 4047 line also remained). The λ 2537 radiation was obtained with great intensity from a water-cooled horizontal quartz mercury arc placed between the poles of an electromagnet. It was monochromatized by passage through an aqueous solution of cobalt and nickel sulphates kept in a cell with fused quartz windows. This filter transmitted a small amount of red light, as well as λ 3100. But these were very feeble in comparison with the λ 2537 radiation.

The monochromatized radiation, limited by a small aperture placed just above the arc, was reflected normally on to the crystal by means of a plate of fused quartz. The interference fringes formed in the crystal were photographed by a camera using a low aperture quartz lens. The fringes were first obtained visually for the λ 5461 radiation. On now altering the focus of the camera, the adjustments were found to be nearly correct for photographing the fringes, and slight shifts of the crystal and the reflecting plate were all that were necessary to obtain the fringes with the maximum clarity. Ilford Process plates were used for photography. These gave good contrast and further, they were insensitive to the red light let through by the filters.

The technique adopted for determining the shift of these fringes was as follows: A number of photographs of the fringes were taken at every two degrees till one complete fringe shift had taken place. With the crystal thicknesses employed, this meant a total temperature shift of about 10° C., or 5 photographs. Sets of photographs like this were taken at 50° intervals up to 400° C. These photographs gave an approximate value of the rate of shift of the fringes with temperature, $\Delta N/\Delta t$. Having obtained these values, it was now easy to take by trial a number of photographs such that a very nearly integral number of fringes (5 or 6) had shifted between two successive photographs. The fractional part of the fringe shift could be estimated to a tenth of a fringe by comparison with the preliminary photographs. In this way $\Delta N/\Delta t$ was accurately determined over the whole range from 50° to 400° C. The temperature coefficient could then be evaluated from the relation

$$\frac{dn}{dt} = \frac{\lambda}{2l}\frac{\Delta N}{\Delta t} - n\alpha_t, \qquad (1)$$

where l represents the thickness of the crystal, and α_t its coefficient of thermal expansion perpendicular to the thickness.

In the case of quartz there were two coefficients to be measured corresponding to the ordinary and extraordinary indices. These were obtained by using a plate cut parallel to the optic axis. Polarised light was produced by keeping the quartz plate used for reflecting the light on the crystal at the Brewsterian angle. The crystal was successively mounted with the optic axis parallel and perpendicular to the electric vector of the incident radiation. This method of polarisation was superior to the use of nicols since no intensity was lost by absorption.

In addition to the ultra-violet studies, photographic measurements were also made in the visible region for the wavelengths λ 4047, λ 4916 and λ 5790 of mercury in the case of some of the crystals. These measurements were

carried out by allowing the direct light of the mercury arc to fall on the crystal. The light reflected by the crystal was condensed by an achromatic camera lens arranged so as to cast a focussed image of the crystal on the slit of a Fuess spectrograph. The slit was widened to 3 or 4 mm. Under these conditions, the spectrograph served both as a monochromator and as a camera, sorting out the fringe systems due to the several radiations and recording them simultaneously on the plate. There was some overlap between the fringe systems due to the λ 5770 and λ 5790. But this did not affect the measurements. By taking photographs at a number of temperatures, dn/dt could be evaluated for the various wavelengths.

The results of these studies are presented in the succeeding pages. They are discussed in the light of dispersion formulae for these crystals, some of which have been freshly computed.

3. Results

(*a*) *Lithium Fluoride*

Values of dn/dt at 100° intervals have been previously given by the author (Radhakrishnan, 1950 *a*) for λ 4358, λ 5461 and λ 5893. The present studies give values at 50° intervals for these lines as well as for the wavelengths λ 2537 and λ 3650 (Table I).

Table I

Temperature (deg. C.)	$10^5\alpha_t$	$10^6\, dn/dt$				
		2537	3650	4358	5461	5893
50	3·48	−1·10	−1·20	−1·23	−1·27	−1·27
100	3·65	−1·31	−1·37	−1·42	−1·44	−1·44
150	3·83	−1·45	−1·54	−1·60	−1·61	−1·60
200	4·03	−1·67	−1·75	−1·81	−1·81	−1·82
250	4·24	−2·00	−1·95	−2·01	−2·03	−2·03
300	4·46	−2·23	−2·20	−2·25	−2·26	−2·27
350	4·69	−2·44	−2·51	−2·56	−2·56	−2·58
400	4·93	−2·65	−2·78	−2·80	−2·82	−2·85

In a previous paper (Radhakrishnan, 1950 *a*), the author has given a dispersion formula for lithium fluoride employing an ultra-violet frequency at λ 914 and an infra-red frequency at 33 μ. Applying Ramachandran's theory of thermo-optic behaviour to this formula (Ramachandran, 1947 *a*), one obtains the result

$$2n\frac{dn}{dt}+\gamma_t(n^2-1)=\frac{17,465}{(122\cdot8-\nu^2)^2}\chi_t \qquad (2)$$

where $$\chi_t = -\frac{1}{\nu_0}\frac{d\nu_0}{dt} \qquad (3)$$

is the proportional rate of change of the ultra-violet frequency with temperature and γ_t is the coefficient of volume expansion of the substance at temperature t. The numerical evaluation of x_t from equation (2) gives the results shown below. The values of γ_t have been taken from the work of Eucken and Danöhl (1934).

TABLE II

Temperature (deg. C.)	$10^5\chi_t$		
	2537	3650	5461
50	5·1	5·1	5·0
100	4·9	5·1	5·0
150	5·0	5·1	5·0
200	5·0	5·1	5·1
250	4·8	5·1	5·0
300	4·9	5·1	5·0
350	5·1	4·9	5·1
400	5·1	4·9	4·8

The constancy of χ shows the validity of equation (2) over the whole range of wavelengths. It is further seen that χ_t is practically unchanged with increasing temperature for lithium fluoride.

(*b*) *Fluorspar*

The temperature coefficient of refraction of fluorspar has been studied by Micheli (1902) at 60° C. in the ultra-violet and visible regions and by Reed (1898) at higher temperatures in the visible region. Table III gives

TABLE III

Temperature (deg. C.)	$10^5\alpha_t$	$10^5\, dn/dt$					
		2537	3650	4358	5461	5893	
						Author	Reed
50	1·93	−0·88	−1·08	−1·10	−1·14	−1·18	−1·19
100	2·02	−0·95	−1·10		−1·19	−1·24	−1·24
150	2·12	−1·02	−1·18		−1·25	−1·31	−1·31
200	2·24	−1·13	−1·29		−1·34	−1·39	−1·37
250	2·36	−1·15	−1·46		−1·44	−1·48	−1·43
300	2·49	−1·36	−1·54		−1·55	−1·59	−1·50
350	2·63	−1·44	−1·56		−1·68	−1·71	−1·56
400	2·79	−1·54	−1·73		−1·83	−1·88	

the author's measurements. Although agreeing with Reed's data at the lower temperatures, they differ more and more from it at higher temperatures. It is significant to note in this connection that a comparison of Reed's work on quartz with that of other investigators shows some systematic discrepancy in the measurement of temperature (Sosman, 1927).

Using Micheli's and Reed's measurements of dn/dt, as well as the thermal expansion values available at that time, Ramachandran (1947 *c*) calculated the temperature shifts in the ultra-violet absorptions of fluorspar. But the author's present work fails to agree with that of Reed, while the thermal expansion values used by Ramachandran are now known to be slightly in error (Sharma, 1950). Consequently the author has repeated Ramachandran's calculations with the better data. The electronic frequencies of fluorspar are known to be at λ 900 and λ 1115. Ramachandran's analysis of Micheli's data shows that the χ values of these frequencies at 60° C. are respectively $1{\cdot}1\times10^{-5}$ and $7{\cdot}0\times10^{-5}$. To calculate χ_t at high temperatures separately for the two frequencies, one requires data on dn/dt extending upto λ 2000. In the absence of such data, one can perform an approximate calculation, as was done by Ramachandran, by replacing the terms at λ 900 and λ 1115 by a weighted mean which lies at λ 943. Ramachandran obtained for this term a χ value of $3{\cdot}3\times10^{-5}$ and found that this value was independent of temperature. But the calculations with the new data on thermal expansion and dn/dt show that χ_t does vary with temperature, as seen in Table IV.

TABLE IV

Temperature (deg. C.)	$10^5\chi_t$			
	2537	3650	5461	5893
50	3·0	2·9	2·9	3·1
100	3·1	3·1	3·1	3·2
150	3·2	3·2	3·2	3·3
200	3·3	3·3	3·4	3·5
250	3·4	3·3	3·5	3·7
300	3·5	3·5	3·6	3·8
350	3·7	3·8	3·7	3·9
400	3·9	3·9	3·9	4·1

Again the constancy of χ in each row of the table shows the validity of the theory. The value of χ_t is found to increase with temperature as is the case with most crystals.

(*c*) *Magnesium Oxide*

Observations with magnesia could not be carried out for the 2537 radiation owing to the low transparency of the crystal for this wavelength. The results for the other radiations are set out in Table V. The thermal expansion values have been taken from the work of Thilenius and Holzmann (1930).

TABLE V

Temperature (deg. C.)	$10^5\alpha_t$	$10^5 dn/dt$				
		3650	4047	4358	5461	5893
50	1·12	1·95	1·85	1·79	1·65	1·60
100	1·16	1·96		1·78	1·64	1·61
150	1·195	1·99		1·80	1·65	1·59
200	1·235	1·99		1·77	1·65	1·61
250	1·29	1·97		1·77	1·64	1·60
300	1·345	1·94		1·78	1·64	1·61
350	1·39	1·95		1·80	1·65	1·60
400	1·41	1·99		1·79	1·65	1·61

A dispersion formula for magnesium oxide has been proposed by the author (Radhakrishnan, 1950 *b*) employing a single ultra-violet term at $\lambda 1180$. The formula for χ_t obtained from the dispersion constants is

$$2n\frac{dn}{dt} + \gamma_t (n^2 - 1) = \frac{16{,}940}{(72 \cdot 10 - \nu^2)^2}\chi_t. \qquad (4)$$

The values of x_t are displayed in Table VI, which verifies the correctness of this equation at each temperature.

TABLE VI

Temperature (deg. C.)	$10^5\chi_t$			
	3650	4358	5461	5893
50	3·48	3·50	3·52	3·46
100	3·55	3·56	3·58	3·52
150	3·62	3·63	3·62	3·56
200	3·69	3·67	3·70	3·65
250	3·76	3·76	3·79	3·74
300	3·83	3·86	3·89	3·81
350	3·90	3·95	3·96	3·90
400	3·97	3·97	3·99	3·94

In the author's earlier paper on magnesium oxide, an error had crept into the calculation of χ_t, the values having been divided throughout by $2n$. This mistake has now been rectified. It is seen that χ_t increases slightly with temperature.

(*d*) *Quartz*

The case of quartz has been studied in detail. Previous experimental measurements by Micheli give the values of dn/dt from 2000 Å to 6500 Å at 60° C. At higher temperatures, values in the visible region have been given by Reed and by Rinne and Kolb (1910). The author's measurements in the visible region are, as in the case of fluorspar, slightly different from those of Reed. The necessary data on thermal expansion were taken from Sosman's book "The Properties of Silica". The measured values of dn_ω/dt and dn_ϵ/dt) are shown in Tables VII and VIII.

TABLE VII

Temperature (deg. C.)	$-10^5 dn_\omega/dt$							
	2537	3650	4047	4358	4916	5461	5790	5893
50	0·29	0·54	0·56	0·59	0·60	0·62	0·62	0·63
100	0·32	0·57		0·65		0·68		0·69
150	0·39	0·65		0·70		0·74		0·75
200	0·43	0·71		0·77		0·82		0·84
250	0·50	0·80		0·85		0·92		0·94
300	0·64	0·95		1·00		1·05		1·08
350	0·78	1·10		1·10		1·20		1·23
400	1·00	1·32		1·24		1·44		1·46

TABLE VIII

Temperature (deg. C.)	$-10^5 dn\epsilon/dt$							
	2537	3650	4047	4358	4916	5461	5790	5893
50	0·40	0·62	0·65	0·66	0·70	0·70	0·71	0·71
100	0·43	0·68		0·74		0·77		0·80
150	0·52	0·77		0·84		0·89		0·91
200	0·55	0·80		0·92		1·00		1·10
250	0·62	0·93		1·01		1·10		1·12
300	0·75	1·12		1·09		1·20		1·23
350	0·89	1·27		1·25		1·35		1·38
400	1·20	1·47		1·58		1·65		1·67

Dispersion formulæ of the Ketteler-Helmholtz form were previously offered by the author for quartz (Radhakrishnan, 1947 *a*), in which the observed infra-red and ultra-violet absorption frequencies were used for the first time. These formulæ fit the data better than any previous formula proposed for quartz. Even this agreement, however, is not as good as could be desired. An additional defect of the formulæ is that they employ a hypothetical ultra-violet term at λ 330 (taken over from previous work by Lowry and Coode-Adams in 1927), the strength of which is very high. On account of this the formulae, when converted to the Drude form, give expressions like

$$n^2 - 1 = -2 + \sum_r \frac{a_r \lambda^2}{\lambda^2 - \lambda_r^2},$$

which is absurd as it leads to a negative strength for some frequency. This defect is now removed by altering the position of the remote ultra-violet term to λ 600. It has then the requisite dispersion with a reasonably low strength. On making this change and reclaculating the oscillator strengths, formulæ have resulted which fit the facts with very good accuracy. These formulæ and their agreement with the facts are given below.

$$n_\omega^2 - 1 = \frac{0{\cdot}663044\,\lambda^2}{\lambda^2 - (0{\cdot}0600)^2} + \frac{0{\cdot}517852\,\lambda^2}{\lambda^2 - (0{\cdot}1060)^2} + \frac{0{\cdot}175912\,\lambda^2}{\lambda^2 - (0{\cdot}1190)^2} + \frac{0{\cdot}565380\,\lambda^2}{\lambda^2 - (8{\cdot}844)^2} + \frac{1{\cdot}675299\,\lambda^2}{\lambda^2 - (20{\cdot}742)^2} \quad (5)$$

$$n_e^2 - 1 = \frac{0{\cdot}665721\,\lambda^2}{\lambda^2 - (0{\cdot}0600)^2} + \frac{0{\cdot}503511\,\lambda^2}{\lambda^2 - (0{\cdot}1060)^2} + \frac{0{\cdot}214792\,\lambda^2}{\lambda^2 - (0{\cdot}1190)^2} + \frac{0{\cdot}539173\,\lambda^2}{\lambda^2 - (8{\cdot}792)^2} + \frac{1{\cdot}807613\,\lambda^2}{\lambda^2 - (19{\cdot}70)^2} \quad (6)$$

TABLE IX

Refractive Indices of quartz in air at 18° C. against I.A.U.

λ (in μ)	n_ω (calc.)	n_ω (obs.)	n_e (calc.)	n_e (obs.)
0·185467	1·67578	1·67578	1·68997	1·68997
0·193583	1·65995	1·65999	1·67343	1·67343
0·214439	1·63045	1·63039	1·64269	1·64262
0·257304	1·59622	1·59622	1·60714	1·60714
0·325253	1·57091	1·57091	1·58091	1·58095
0·396848	1·55812	1·55813	1·56770	1·56772
0·486133	1·54968	1·54968	1·55898	1·55898
0·546072	1·54617	1·54617	1·55535	1·55535
0·656278	1·54191	1·54190	1·55094	1·55093
0·706520	1·54051	1·54049	1·54949	1·54947

Refractive indices in the infra-red have been omitted from this table, since their representation is the same as in the author's previous paper. It is seen that the terms at λ 600 and λ 1060 are nearly the same for both the indices. Most of the birefringence arises from the term at λ 1190.

Passing now to the consideration of dn/dt, the data were previously explained by the author (1947 *b*) as due to a change of density and a shift in the absorption frequency, without specifically taking into account the anisotropy of the crystal. The terms at λ 1190 and λ 1060 were replaced by a weighted mean at λ 1127 having a mean χ of $3{\cdot}0\times10^{-5}$ at 60° C. Since rigorous dispersion formulæ have now been evolved, which express the anisotropies of the terms completely, it is possible to calculate the values of the various terms separately, as well as the contribution of the anisotropy factor to dn/dt. Ramachandran (1948) has shown that in a uniaxial crystal, dn/dt can be expressed for both the rays in a form which is equivalent to the formulæ

$$\left.\begin{aligned} f_\omega &= 2n_\omega \frac{dn_\omega}{dt} + \gamma_t (n_\omega{}^2 - 1) = \sum_i \left[\tfrac{1}{2} (\alpha_\perp - \alpha_{||}) \frac{Q_i}{\nu_i{}^2 - \nu^2} + \frac{2b_{\omega i}\, \nu_i{}^4\, \chi_i}{(\nu_i{}^2 - \nu^2)^2} \right] \\ f_\epsilon &= 2n_\epsilon \frac{dn_\epsilon}{dt} + \gamma_t (n_\epsilon{}^2 - 1) = \sum_i \left[-(\alpha_\perp - \alpha_{||}) \frac{Q_i}{\nu_i{}^2 - \nu^2} + \frac{2b_{\epsilon i}\, \nu_i{}^4\, \chi_i}{(\nu_i{}^2 - \nu^2)^2} \right] \end{aligned}\right\} \quad (7)$$

The Q's represent a directional transfer of the strengths of the individual absorptions in such a manner that the total strength remains constant. The constants $b_{\omega i}$ and $b_{\epsilon i}$ are merely the dispersion constants appearing in the numerators of the dispersion formulæ, and χ_i is the proportional rate of change of each electronic frequency with temperature. The infra-red frequencies are neglected in this picture since they offer only slight contributions to dn/dt in the ultra-violet and visible regions. On evaluating the Q and χ for the various frequencies at 60° C., using Micheli's data, one obtains the following results:—

$$Q\,(600) \gtrsim 0;\quad Q\,(1060) \gtrsim 0;\quad Q\,(1190) = 62{\cdot}3$$

$$\chi\,(600) \gtrsim 0;\quad \chi\,(1060) \gtrsim 0;\quad \chi\,(1190) = 7{\cdot}8\times10^{-5}$$

Thus the terms at λ 600 and λ 1060 undergo practically no directional transfer in strength. This is to be expected since their anisotropies are very slight. But the strongly anisotropic term at λ 1190 has a transfer coefficient of 62·3, which when expressed in Ramachandran's notation leads to a value of 0·882 for his $K = Q/\nu_0{}^2$. The order of this transfer coefficient is the same as in other anisotropic crystals, for example calcite, for which Ramachandran obtains $K = 1{\cdot}006$. When there are three Q's and three χ's to fix, it is difficult to assign unambiguous numerical values to all of them. One can assign a small Q and a small χ to the λ 1060 term and still retain a good fit with facts.

The calculated values of the temperature coefficients using Equation (7) are compared with the experimental values in Table X.

TABLE X

Wavelength A.U.	$10^5 dn_\omega/dt$ (calc.)	$10^5 \frac{dn_\omega}{dt}$ (obs.)	$10^5 \frac{dn_\varepsilon}{dt}$ (calc.)	$10^5 \frac{dn_\varepsilon}{dt}$ (obs.)
2026	+0·12	+0·18	+0·10	+0·13
2063	+0·06	+0·12	+0·03	+0·06
2144	−0·01	−0·01	−0·05	−0·05
2195	−0·07	−0·06	−0·13	−0·11
2265	−0·17	−0·14	−0·19	−0·20
2313	−0·18	−0·18	−0·24	−0·24
2573	−0·31	−0·31	−0·40	−0·39
2981	−0·43	−0·43	−0·53	−0·53
3613	−0·53	−0·53	−0·63	−0·64
4800	−0·59	−0·61	−0·70	−0·72
5893	−0·62	−0·65	−0·73	−0·75
6438	−0·63	−0·66	−0·74	−0·76

The fit with the experimental data appears unsatisfactory at the lowest wavelengths. But it must be remembered that dn/dt is really the net effect of two large quantities of opposite sign, namely, contributions due to volume and frequency changes. Our formulæ are developed in a form which expresses not the net effect, but the contribution due to frequency changes alone. Since this quantity has several times the magnitude of dn/dt, a small error in its representation results in large errors in the calculated value of dn/dt.

To calculate χ_t at higher temperatures, one assumes that Q is the same at different temperatures, *i.e.*, that the transfer is proportional to the difference in the linear thermal expansions parallel and perpendicular to the optic axis. χ_t can then be evaluated from equation (7) using the known values of $\alpha_\perp$, $\alpha_{||}$ and γ_t (Sosman, 1927). The values of χ_t are given below:

TABLE XI

Temperature (deg. C.)	$10^5\gamma_t$	$10^5 \times (\alpha_\perp - \alpha_{||})$	$10^5\chi_t$			$10^5\chi_t$		
			Ordinary Ray			Extraordinary Ray		
			2537	3650	5461	2537	3650	5461
50	3·68	0·65	7·7	7·4	7·4	7·7	7·7	7·7
100	4·00	0·68	8·3	8·2	7·9	8·3	8·3	8·3
200	4·66	0·75	9·4	9·3	9·0	9·4	9·5	8·9
300	5·49	0·82	10·4	10·2	10·1	10·5	10·1	10·2
400	6·74	0·88	11·7	11·6	11·3	11·3	11·5	11·1

The approximate constancy of the value of χ shows the validity of the assumptions made in the theory.

The results obtained generally indicate that χ_t varies by 50 per cent. from room temperature to 400° C. Taking the weighted mean of the χ for the 1190 and 1060 terms, we obtain a value of $2{\cdot}5\times10^{-5}$ for the electronic absorptions at 50° C. This is precisely the χ value obtained by Ramachandran (1947 *b*) for fused quartz, working with a single term at λ 1070. In view of Tousey's observations (1940) of two peaks in the reflection spectrum of both crystal quartz and fused quartz at λ 1060 and λ 1190, the one-term formula used by Ramachandran has to be considered as only a weighted mean. Thus there is a striking similarity between quartz and vitreous silica as regards the positions and the temperature shifts of the electronic lines. This similarity also holds at higher temperatures.

(*e*) *Barite*

Barite is an orthorhombic crystal having three principal refractive indices n_α, n_β and n_γ. These three indices respectively correspond to the electric vector parallel to the crystallographic axes *c*, *b* and *a*. The temperature coefficients of n_β and n_γ were evaluated from observations on a cleavage plate parallel to the *c* (001) face. The coefficient dn_α/dt was obtained by observations on another cleavage plate parallel to the *m* (110) face and using polarised light with the electric vector parallel to the *c*-axis. The refractive index for light with the electric vector in the plane of the plate and perpendicular to the *c*-axis is given by n_m where

$$n_m^{-2} = \cos^2\theta \cdot n_\beta^{-2} + \sin^2\theta \cdot n_\gamma^{-2}$$

and θ is the angle between the electric vector of n_m and the *b*-axis. On differentiating this with respect to temperature and neglecting the small correction caused by the change in θ with temperature, one obtains

$$dn_m/dt = 0{\cdot}60\, dn_\beta/dt + 0{\cdot}39\, du_\gamma/dt\,. \qquad (8)$$

This formula provided a check on the internal accuracy of the experiment, since dn_m/dt could be measured and compared with the values calculated from dn_β/dt and dn_γ/dt. The relevant thermal expansion data were taken from the work of Sharma (1950) (under publication). The four coefficients in the case of the λ 5461 radiation are given in Table XII:

The dispersion of barite has been measured only in the visible region. Consequently, accurate dispersion formulæ cannot be constructed for this

TABLE XII

Temperature (deg. C.)	$10^5\alpha_c$	$10^5\alpha_m$	$-10^5\, dn/dt$				
			α	β	γ	m (obs.)	m(calc.)
50	1·49	1·84	2·13	1·82	2·53	2·05	2·07
100	1·57	1·91	2·19	1·90	2·62	2·13	2·16
150	1·66	1·98	2·23	2·00	2·73	2·20	2·27
200	1·76	2·07	2·29	2·12	2·83	2·30	2·37
250	1·86	2·16	2·35	2·23	2·93	2·37	2·44
300	1·96	2·26	2·44	2·35	3·04	2·50	2·59
350	2·07	2·36	2·52	2·46	3·14	2·60	2·69
400	2·19	2·48	2·67	2·60	3·25	2·78	2·83

crystal. One-term formulæ can, however, be obtained with a dispersion frequency at λ 1000. These formulæ are of the type

$$n_i^2 - 1 = a_i + \frac{b_i \lambda^2}{\lambda^2 - 0{\cdot}0100}, \tag{9}$$

where the constants a_i and b_i are given below. The fit is fairly good as seen from Table XIII:

Ray	a_i	b_i
α	0·1982	1·4362
β	0·1828	1·4549
γ	0·1361	1·5354

TABLE XIII

Wavelength	n_α (calc.)	n_α (obs.)	n_β (cal.)	n_β (obs.)	n_γ (calc.)	n_γ (obs.)
a 0·71890	1·6318	1·6318	1·6329	1·6329	1·6437	1·6437
C 0·65628	1·6337	1·6336	1·6347	1·6346	1·6456	1·6456
D 0·58959	1·6362	1·6361	1·6373	1·6373	1·6483	1·6484
F 0·48613	1·6425	1·6427	1·6442	1·6442	1·6551	1·6551
G 0·43079	1·6481	1·6481	1·6494	1·6494	1·6610	1·6607
H 0·39685	1·6528	1·6528	1·6542	1·6543	1·6660	1·6660

With such elementary formulæ, it is not possible to make a detailed analysis of the temperature coefficient in terms of oscillator transfer and changes in electronic frequencies. But one can obtain an idea of the magnitude of χ by forming the functions

$$f_i = 2n_i \frac{dn_i}{dt} + \gamma_t (n_i^2 - 1); \quad i = \alpha,\ \beta,\ \gamma \tag{10}$$

From Ramachandran's theory, the sum of these functions is

$$f_\alpha + f_\beta + f_\gamma = \frac{2\,(b_\alpha + b_\beta + b_\gamma)}{(\nu_0^2 - \nu^2)^2}\,\nu_0^4\,\chi_t \qquad (11)$$

and the transfer term becomes identically equal to zero. The values of χ_t obtained in this way are given in Table XIV:

TABLE XIV

Temp. (deg. C.)	$10^5\gamma_t$	$10^5\chi_t$
100	2·24	0·80
200	2·41	0·92
300	2·61	1·05
400	2·84	1·19

As usual, χ_t is found to increase with temperature.

The author expresses here his thanks to Professor R. S. Krishnan and Dr. G. N. Ramachandran for their guidance and encouragement during the course of this work.

SUMMARY

The temperature coefficients of refraction of lithium fluoride, fluorspar, magnesia and quartz have been determined interferometrically for wavelengths between λ 2500 and λ 6000, from room temperature to 400° C. The values have been utilised, in conjunction with dispersion formulæ mostly proposed by the author, to calculate the temperature dependence of the ultra-violet frequencies, using Ramachandran's theory of thermo-optic behaviour. The theory is found to account successfully for the variation of dn/dt with wavelength and temperature. Similar results have been obtained in the visible region alone for the three refractive indices of barite.

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A NEW SYNTHESIS OF THIOPHENES AND THIAPYRANS

Part III. Hydroxythionaphthenes and Alkoxythionaphthenes

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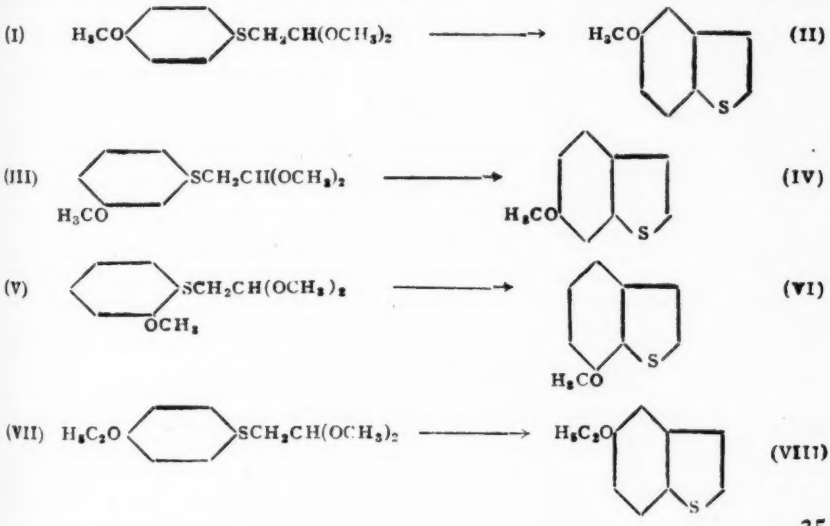
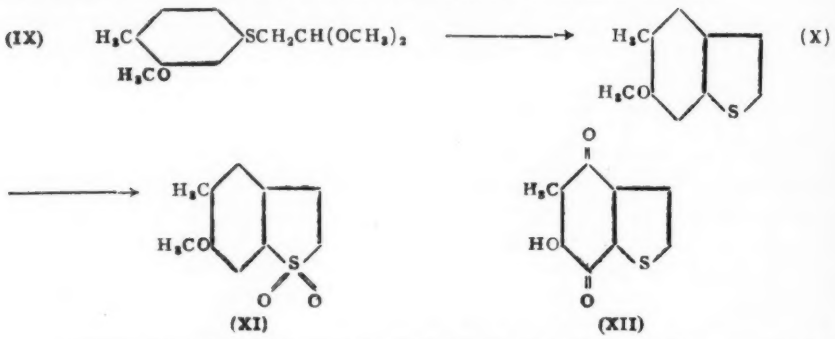
Of the six possible monomethoxythionaphthenes only 3-methoxy-[1] and 5-methoxy-thionaphthenes[2] are known and are obtained by methylation of the corresponding hydroxy derivatives. Out of the remaining four unknown monomethoxythionaphthenes, 6-methoxy- (IV) and 7-methoxy-thionaphthenes (VI) have now been prepared in addition to 5-methoxythionaphthene (II), now prepared by an alternative route. Among the monoethoxythionaphthenes only the 3-ethoxy derivative[3] is reported. 5-Ethoxythionaphthene has now been synthesised.

5-Methoxythionaphthene (II) was prepared starting from *p*-mercaptoanisole by condensation with bromoacetaldehyde dimethyl acetal to give *p*-methoxyphenyl ω-dimethoxyethyl sulphide (I) followed by ring-closure of the latter to (II). 6-Methoxythionaphthene (IV) was prepared similarly by the cyclization of *m*-methoxyphenyl ω-dimethoxyethyl sulphide (III). 7-Methoxythionaphthene (VI) was likewise obtained from *o*-methoxyphenyl



ω-dimethoxyethyl sulphide (V). Cyclization of *p*-ethoxyphenyl ω-dimethoxyethyl sulphide (VII) gave 5-ethoxythionaphthene (VIII). The yield of the latter was more than that of 5-methoxythionaphthene (II). The yield of (IV) (62%) was more than that of (VI) (18%), because of the activation of the cyclization position due to the *p*-methoxy group.

6-Methoxy-5-methylthionaphthene (X) was prepared by the cyclization of 3-methoxy-4-methylphenyl ω-dimethoxyethyl sulphide (IX) as an intermediate in the synthesis of the sulphur isoster (XII) of the physiologically active 3-hydroxy-2-methyl-1 : 4-naphthoquinone (" phthiacol ") and also with the view to illustrate the application of the new synthesis to disubstituted derivatives of thionaphthene. Oxidation of (X) with hydrogen peroxide in acetic acid gave 6-methoxy-5-methylthionaphthene-1-dioxide (XI).



Among the monohydroxythionaphthenes, 2-hydroxy-[4], 3-hydroxy-(thioindoxyl),[5] 4-hydroxy-[6] and 5-hydroxy-thionaphthenes [2,6] are known. Demethylation of 7-methoxythionaphthene (VI) by treatment with pyridine hydrochloride[7] at 180° for 8 hours gave 7-hydroxythionaphthene (XIII) in 88% yield. Even after repeated distillations under reduced pressure, the hydroxy derivative did not give correct elementary analysis. It distils as a colourless liquid which solidifies on cooling to a white solid and darkens on keeping. It dissolves in aqueous alkali, couples with benzenediazonium chloride giving a chocolate-coloured dye. The hydroxythionaphthene crystallized from *n*-hexane in colourless fluffy needles, m.p. 67–68°, which on keeping in an evacuated desiccator overnight changed to a colourless oil. The hydroxy derivative is being investigated further.

Demethylation of (X) gave 6-hydroxy-5-methylthionaphthene (XIV) in 85% yield. The hydroxythionaphthene coupled with benzenediazonium chloride giving a reddish-brown dye.

Experimental

(Analyses are by Drs. Weiler and Strauss and by Mr. T. S. Gore. M.ps. are uncorrected.)

The condensation of alkoxyphenylthiols with bromoacetaldehyde dimethyl acetal, the subsequent cyclization of *S*-alkoxyphenylthioglycollicaldehyde dimethyl acetals to the corresponding alkoxythionaphthenes and the characterization of the intermediate acetals as 2:4-dinitrophenylhydrazones have been carried out according to the general method outlined earlier.[8] The thionaphthenes were characterised as the picrates.

p-*Methoxyphenyl ω-dimethoxyethyl sulphide* (*I*)

p-*Mercaptoanisol*[9] (7·6 g.), sodium (1·2 g.), sodium iodide (1·25 g.), bromoacetal (9·3 g.) and absolute alcohol (25 c.c.) were boiled for 2 hours. The crude sulphide after distillation, gave a colourless liquid, b.p. 170–80° (bath temp.)/2·5–3 mm. (8·6 g.; yield 70%). After three redistillations it was collected at 155–60° (bath temp.)/2·5–3 mm. (Found: C, 58·2; H, 7·0. $C_{11}H_{16}O_3S$ requires C, 57·9; H, 7·0%). 2:4-*Dinitrophenylhydrazone* crystallized from alcohol in lustrous flat orange needles, m.p. 106–07° (Found: N, 16·1. $C_{15}H_{14}N_4O_5S$ requires N, 15·5%).

5-*Methoxythionaphthene* (*II*)

The sulphide (I) (6·1 g.) was added to phosphorus pentoxide (30 g.) and phosphoric acid (18 c.c.) at 150–60°/0·34 mm. 5-Methoxythionaphthene was isolated through the picrate and distilled when it was obtained as a white solid having a pleasant smell, m.p. 42–43°; b.p. 85–90° (bath temp.)/0·52 mm. Fries *et al.*[2] give m.p. 44° (Found: C, 66·0; H, 4·9. Calc. for C_9H_8OS: C, 65·9; H, 4·9%). The yield of 5-methoxythionaphthene was poor.

m-*Methoxyphenyl ω-dimethoxyethyl sulphide* (*III*)

m-Mercaptoanisol[10] (6·1 g.), sodium (1·0 g.), sodium iodide (1·0 g.), bromoacetal (7·4 g.) and absolute alcohol (30 c.c.) were boiled for 3 hours. The sulphide gave a colourless liquid, b.p. 120–60° (bath temp.)/2·5 mm. (7·31 g.; yield 74%). After three redistillations it was finally collected at 125–30° (bath temp.)/2·5 mm. (Found: C, 57·2; H, 7·0. $C_{11}H_{16}O_3S$ requires C, 57·9; H, 7·0%). 2:4-*Dinitrophenylhydrazone* gave small yellow

rods (alcohol-benzene, m.p. 123–24° (Found: N, 15·2. $C_{15}H_{14}N_4O_5S$ requires N, 15·5%).

6-*Methoxythionaphthene* (*IV*)

The sulphide (VII) (4·13 g.) was added to a mixture of phosphorous pentoxide (20 g.) and phosphoric acid (12 c.c.) at 160–70°/2·5 mm. Crude 6-methoxythionaphthene (1·84 g., yield 62%) was isolated through the picrate and the purified product (0·88 g.) was finally distilled twice when it gave a colourless liquid, b.p. 153–56° (bath temp.)/16 mm. (Found: C, 65·8; H, 5·1. C_9H_8OS requires C, 65·9; H, 4·9%). The *picrate* crystallised in yellow needles from alcohol, m.p. 105–06° (Found: N, 11·3. $C_{15}H_{11}N_3O_8S$ requires N, 10·7%).

o-*Methoxyphenyl ω-dimethoxyethyl sulphide* (*V*)

o-Mercaptoanisole (6 g.), prepared from *o*-anisidine (*cf.*, preparation of *m*-thiocresol),[11] sodium (1 g.), bromoacetal (7·5 g.) and absolute alcohol (30 c.c.) were boiled for 6 hours. The crude sulphide after distillation, gave a pale yellow liquid, b.p. 150–80° (bath temp.)/15 mm. (8·0 g; yield 82%). After three redistillations it was collected at 175–80° (bath temp.)/15 mm. (Found: C, 57·4; H, 6·8. $C_{11}H_{16}O_3S$ requires C, 57·9; H, 7·0%). 2:4-*Dinitrophenylhydrazone* crystallized from alcohol in orange needles, m.p. 135–36° (Found: N, 15·3. $C_{15}H_{14}N_4O_5S$ requires N, 15·5%).

7-*Methoxythionaphthene* (*VI*)

The sulphide (V) (6·25 g.) was added to a mixture of phosphorus pentoxide (31 g.) and phosphoric acid (20 c.c.) at 160–70°/15 mm. when a pale yellow liquid (0·8 g.; yield 18%) was obtained. It was treated with picric acid (1·2 g.) and the picrate was decomposed by passing a benzene solution through a column of activated alumina. The fraction which gave blue fluorescence in ultra-violet light, was collected and gave the thionaphthene as a colourless liquid. The liquid was redistilled thrice and finally collected at 140–45° (bath temp.)/15 mm. (Found: C, 65·9; H, 4·9. C_9H_8OS requires C, 65·9; H, 4·9%). The *picrate* crystallised in elongated orange needles from absolute alcohol, m.p. 110–11° (Found: N, 10·4; $C_{15}H_{11}N_3O_8S$ requires N, 10·7%).

p-*Ethoxyphenyl ω-dimethoxyethyl sulphide* (*VII*)

p-Mercaptophenetol (10·7 g.), prepared from *p*-phenetidine (*cf.*, preparation of *m*-thiocresol),[11] sodium (1·6 g.) bromoacetal (13·4 g.) and absolute alcohol (50 c.c.) were refluxed for 3 hours. The sulphide gave a pale yellow

liquid, b.p. 180–85°/16 mm. (14·2 g.; yield 85%). After three redistillations, it was collected at 180° (bath temp.)/12 mm. (Found: C, 59·5; H, 7·4. $C_{12}H_{18}O_3S$ requires C, 59·5; H, 7·4%). 2:4-*Dinitrophenylhydrazone* crystallized from alcohol with one molecule of alcohol of crystallization in orange needles, m.p. 84–85° (Found: N, 13·5. $C_{16}H_{16}N_4O_5S$, C_2H_5OH requires N, 13·3%).

5-*Ethoxythionaphthene* (*VIII*)

The sulphide (VII) (8·5 g.) was added to a mixture of phosphorus pentoxide (42 g.) and phosphoric acid (25·5 c.c.) at 180–200°/12 mm. The yellow liquid (0·96 g.; yield 15·4%) was treated with picric acid (1·25 g.) in absolute alcohol. The picrate was dissolved in benzene and the solution passed through an activated alumina column using benzene for developing the chromotogram. The fraction, which exhibits a bluish-green fluorescence in ultra-violet light, was collected and gave the thionaphthene as a liquid possessing a fruity smell. The liquid was redistilled four times and finally collected at 145° (bath temp.)/12 mm. (Found: C, 67·3; H, 5·7. $C_{10}H_{10}OS$ requires C, 67·4; H, 5·6%). The *picrate* crystallized in yellow needles from absolute alcohol, m.p. 93° (Found: N, 10·6. $C_{16}H_{13}N_3O_8S$ requires N, 10·3%).

4-Nitro-2-methoxytoluene was prepared from 4-nitro-*o*-toluidine (Fast Scarlet G Base) by Sandmeyer reaction and methylation of the resulting *p*-nitro-*o*-cresol. 4-Nitro-2-methoxytoluene (20 g.) was dissolved in absolute alcohol (100 c.c.), Raney nickel (2 g.) was added and the mixture shaken in a Parr hydrogenator with hydrogen for 4–5 hours at 42 lb. per sq. inch. Removal of Raney nickel and evaporation of alcohol, gave 4-amino-2-methoxytoluene, as a dark brown solid (14 g.), m.p. 54–56°, which was converted to *o*-methoxy-*p*-thiocresol, b.p. 130° (bath temp.)/12 mm. (*cf.*, preparation of *m*-thiocresol from *m*-toluidine).[11] The thiol has been prepared earlier by Shah, *et al.* by reduction of 2-methoxytoluene-4-sulphonyl chloride.

3-*Methoxy*-4-*methylphenyl ω-dimethoxyethyl sulphide* (*IX*)

o-Methoxy-*p*-thiocresol (8·5 g.), sodium (1·3 g.), bromoacetal (9·5 g.) and absolute alcohol (50 c.c.) were boiled for four hours. The crude sulphide after distillation gave a liquid, b.p. 190–95°/15 mm. (11·2 g.; yield 84%). After four redistillations it was collected at 185° (bath temp.)/15 mm. (Found: C, 59·4; H, 7·6. $C_{12}H_{18}O_3S$ requires C, 59·5; H, 7·4%), 2:4-*Dinitrophenylhydrazone* gave orange needles from benzene-*n*-hexane, m.p. 123–24° (Found: N, 15·1. $C_{16}H_{16}N_4O_5S$ requires N, 14·9%).

6-Methoxy-5-methylthionaphthene (*X*)

The sulphide (IX) (8 g.) was added to a mixture of phosphorus pentoxide (40 g.) and phosphoric acid (25 c.c.) at 200–05°/12 mm. when a colourless liquid (3·6 g.; yield 64%) distilled over which solidified on cooling to room temperature. The product was crystallized from *n*-hexane and then further purified by three redistillations, being finally collected at 160° (bath temp.)/12 mm., m.p. 62–63° (Found: C, 66·9; H, 5·4. $C_{10}H_{10}OS$ requires C, 67·4; H, 5·6%). The *picrate* gave long orange-red needles from absolute alcohol, m.p. 107–8° (Found: N, 10·3. $C_{16}H_{13}N_3O_8S$ requires N, 10·3%).

6-Methoxy-5-methylthionaphthene -1-dioxide(*XI*)

The thionaphthene (X) (0·45 g.) was treated with glacial acetic acid (7 c.c.) and hydrogen peroxide 120 vols. (3 c.c.) on water-bath at 85° for 6 hours. The reaction mixture was poured into crushed ice, and neutralized with potassium carbonate. 6-Methoxy-5-methylthionaphthene-1-dioxide was isolated by means of ether, and crystallized from aqueous alcohol when it gave colourless elongated needles, m.p. 187° (Found: C, 57·1; H, 5·2. $C_{10}H_{10}O_3S$ requires C, 57·1; H, 4·8%).

7-Hydroxythionaphthene (*XII*)

7-Methoxythionaphthene (0·62 g.) and pyridine hydrochloride (5 g.) were heated at 180° for 9 hours. The mixture was diluted with ice-cold water and extracted with ether. The ether solution was extracted with 10% caustic soda solution to remove 7-hydroxythionaphthene from the unreacted 7-methoxythionaphthene. The alkaline extract was acidified and the hydroxythionaphthene isolated by means of ether. The ether extract was washed with saturated sodium sulphate solution till free from acid and dried (Na_2SO_4). Removal of ether gave the thionaphthene as a pale straw-coloured liquid (0·5 g; yield 88%). The liquid was distilled four times and finally collected at 135° (bath temp.)/8 mm. as a colourless oil which slowly solidifies, darkens on keeping and does not give correct analysis. The hydroxythionaphthene crystallised from *n*-hexane in colourless fluffy short needles, m.p. 67–68°. On keeping the crystalline product in an evacuated desiccator overnight, a pale yellow-coloured liquid was obtained, which was not analytically pure. A mixture of hydroxythionaphthene (30 mg.) and picric acid (55 mg.) was boiled in absolute alcohol and cooled. The *picrate* separated in elongated orange needles, m.p. 184–86° (Found: C, 44·6; H, 2·7; N, 10·7. $C_{14}H_9N_3O_8S$ requires C, 44·3; H, 2·4; N, 11·1%).

6-Hydroxy-5-methylthionaphthene (XIV)

6-Methoxy-5-methylthionaphthene (0·73 g.) and pyridine hydrochloride (5 g.) were refluxed for 10 hours at 180°. The solution was then diluted with ice-cold water (20 c.c.) and extracted with ether. The ether extract was shaken with 10% caustic soda solution to remove the hydroxythionaphthene. The alkaline extract was acidified and the hydroxy derivative isolated by means of ether. The ether extract was washed with saturated sodium sulphate solution and dried (Na_2SO_4). Removal of ether gave 6-hydroxy-5-methylthionaphthene (0·57 g.; yield 85%) which on distillation gave a colourless liquid, b.p. 160–65° (bath temp.)/10 mm. (0·325 g.) which solidifies at room temperature. The hydroxythionaphthene was crystallized four times from aqueous alcohol when it gave colourless broken plates, m.p. 146–47° (Found: C, 65·6; H, 4·9. C_9H_8OS requires C, 65·8; H, 4·9%).

Summary

5-Methoxythionaphthene (II) and the hitherto unknown 6-methoxy- (IV), 7-methoxy- (VI) and 5-ethoxy-thionaphthenes (VIII) have been prepared by the new synthesis. 6-Methoxy-5-methylthionaphthene (X) was also prepared similarly and gave 6-methoxy-5-methylthionaphthene-1-dioxide (XI) on oxidation. Demethylation of (VI) and (X) gave 7-hydroxythionaphthene (XIII) and 6-hydroxy-5-methylthionaphthene (XIV).

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STUDIES ON THE DEPENDENCE OF OPTICAL ACTIVITY ON CHEMICAL CONSTITUTION*

Part XXXIV. The Camphor-β-sulphonates (*d*-, *l*-, and *dl*-) of *o*-, *m*-, and *p*-Anisidine and of *o*- and *p*-Aminophenol

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IN Parts XXVIII and XXIX of this series of investigations,[1] the rotatory dispersions of salts of camphor-β-sulphonic acid (*d*-, *l*-, and *dl*-) were described. We have included in the present investigation the salts of *o*-, *m*- and *p*-anisidine and *o*- and *p*-aminophenol. One of the objects of the work is to study the effect of substituting the methoxy and hydroxy groups in different positions for a hydrogen atom in the benzene ring of the anilino-camphor-β-sulphonates on the rotatory power of the resulting compounds.

NATURE OF THE ROTATORY DISPERSION

These compounds exhibit simple rotatory dispersion as their rotatory powers can be expressed by Drude's one-term equation. The calculated values of the rotatory power for different wavelengths agree with the observed ones within the limits of experimental error. Tables (IV to VIII) record the observed values of rotatory dispersion of the *d*- and *l*-compounds. The individual calculated values are omitted owing to economy of space. Out of 480 observations, 472 measurements are within the limits of experimental error, namely, 0·02°, in the observed angle of rotation.

THE PHYSICAL IDENTITY OF ENANTIOMERS

The rotatory powers of *d*-, and *l*-forms of the salts of camphor-β-sulphonic acid are identical in all solvents and this lends further support to Pasteur's Principle of Molecular Dissymmetry. Out of 480 observations recorded in this paper, in as many as 434 cases, the differences in the numerical values of the specific rotatory power of the optically active and opposite isomers are within less than 0·01° in the observed angle of rotation and in the remaining 46 cases the angle lies between 0·01° and 0·02° which is within the limits of experimental error allowed in these measurements.

* In the paper with the same title published in Vol. XXX, No. 5, of these *Proceedings*, there were several mistakes. The paper has accordingly been reprinted in the present corrected form.

The Effect of the Solvent on Rotatory Power

The molecular rotatory power, $[M]^{35°}_{5461}$, of the compounds in different solvents is given in Table I. The sequence of decreasing rotatory powers

TABLE I

$[M]^{35°}_{5461}$

No.	Structural formula	Water (80)*	Methyl alcohol (31·2)*	Pyridine (12·4)*	Chloroform (5·2)*
1[c]	$C_{10}H_{15}O.SO_3H.H_2N$–C$_6$H$_4$ (325)[a]	66·63 (11·05)[b]	105·3 (20·43)[b]	123·8 (24·60)[b]	147·2 (30·15)[b]
2	$C_{10}H_{15}O.SO_3H.H_2N$–C$_6$H$_4$(OCH$_3$) (355)[a]	88·74 (16·94)[b]	95·85 (18·26)[b]	106·5 (19·93)[b]	113·6 (22·38)[b]
3	$C_{10}H_{15}O.SO_3H.H_2N$–C$_6$H$_4$(OCH$_3$) (355)[a]	92·30 (18·01)[b]	117·1 (25·99)[b]	117·1 (21·92)[b]	121·5 (23·52)[b]
4	$C_{10}H_{15}O.SO_3H.H_2N$–C$_6$H$_4$–OCH$_3$ (355)[a]	97·61 (18·24)[b]	113·6 (27·19)[b]	106·5 (20·21)[b]	115·3 (22·84)[b]
5	$C_{10}H_{15}O.SO_3H.H_2N$–C$_6$H$_4$(OH) (341)[a]	86·96 (16·04)[b]	95·50 (18·29)[b]	114·2 (22·68)[b]	225·1 (44·36)[b]
6	$C_{10}H_{15}O.SO_3H.H_2N$–C$_6$H$_4$–OH (341)[a]	107·4 (20·32)[b]	116·0 (22·48)[b]	114·2 (22·68)[b]	122·7 (24·12)[b]

* This indicates the Dielectric Constant of the solvent.

(*a*) The values in brackets refer to molecular weights.

(*b*) The values in brackets refer to k_0s, the "absolute" molecular rotation constants.

(*c*) Singh, B. K., and Perti, O. N., *Proc. Ind. Acad. Sci.* (A), 1945, **22**, 267.

of the salts of camphor-β-sulphonic acid in different solvents is given below:

(*a*) o-*Anisidinocamphor-β-sulphonates.*—

chloroform > pyridine > methyl alcohol > water.

The sequence agrees exactly with that of the dielectric constants in the reverse order.

(*b*) m-*Anisidinocamphor-β-sulphonates.*—

chloroform > pyridine = methyl alcohol > water.

The sequence is exactly in the reverse order of the dielectric constants of the solvent except pyridine for which it has become identical with that in methyl alcohol.

(*c*) p-*Anisidinocamphor-β-sulphonates.*—

chloroform > methyl alcohol > pyridine > water.

The sequence is again in the reverse order except for methyl alcohol and pyridine in whose cases the sequence is reversed.

(*d*) o-*Aminophenolcamphor-β-sulphonates.*—

chloroform > pyridine > methyl alcohol > water.

The sequence is again in the reverse order of the dielectric constants of the solvents.

(*e*) p-*Aminophenolcamphor-β-sulphonates.*—

chloroform > methyl alcohol > pyridine > water.

The sequence here is in the reverse order of the dielectric constants except for methyl alcohol and pyridine which are interchanged.

These sequences for the mercury green line (5461) also hold good for other wavelengths.

Nature of the Racemic Modification

The melting points of all the racemic forms are higher than those of their corresponding optical isomers which shows that they are true *dl*-compounds. However, the nature of the racemic form was further confirmed by adding a small amount of the *d*-form to the corresponding racemic form and in each case it was found that the melting point was lowered. This clearly shows that the racemic camphor-β-sulphonates are true *dl*-compounds.

The Molecular Rotatory Power of Camphor-β-Sulphonic Acid Salts in Aqueous Solution and Comparison of the Values of $[M]_{\lambda}^{35°}$ of Camphor-β-Sulphonate Ion in Water

Table II gives the values of $[M]_{\lambda}^{35°}$ for λ varying from 4358 Å.U. to 6708 Å.U. for the different camphor-β-sulphonates in aqueous solution. If the salts are completely ionised in dilute aqueous solution, their molecular

TABLE II

$[M]_{\lambda}^{35°}$ *in aqueous solution for* d-*form*

No	Camphor-β-sulphonates	Li 6708	Cd 6438	Li 6104	Na 5893	Hg 5780	Hg 5461	Ag 5209	Cd 5086	Cd 4800	Cd 4678	Li 4603	Hg 4358
1	*o*-Anisidine ..	49·69	53·25	63·90	70·11	74·54	88·74	102·9	110·1	136·7	150·0	159·7	202·3
2	*m*-Anisidine ..	51·47	57·69	66·55	73·67	78·09	92·30	106·5	115·3	136·7	153·6	164·2	..
3	*p*-Anisidine ..	53·25	60·34	69·21	76·32	81·64	97·61	116·2	126·0	150·9	166·8	179·3	229·0
4	*o*-Aminophenol ..	46·89	52·00	60·53	67·36	71·61	86·96	98·91	107·4	134·7	148·4	158·6	203·8
5	*p*-Aminophenol ..	59·68	66·49	76·74	85·25	90·36	107·4	124·5	136·4	167·1	184·2	197·8	250·7

rotation will be practically the same for a given wavelength, the rotation being independent of the inactive basic ion. In concentrated solution the observed molecular rotation may be greater or less than the value in dilute solution, because it is due both to the active ion and the non-ionised molecule. The results given in Table II show the molecular rotatory power, $[M]_D^{35°}$, of salts of *o*-anisidine as 70·11°, *m*-anisidine 73·67°, *p*-anisidine 76·32°, *o*-aminophenol 67·36° and *p*-aminophenol 85·25°. The molecular rotatory power $[M]_D^{35°}$, of camphor-β-sulphonic acid ion in water being 53-54° at 35°, the above mentioned values of molecular rotations of camphor-β-sulphonates of these bases (Table II) indicate that the undissociated salts have higher rotatory power than the completely dissociated molecule and that, therefore, these salts are not completely ionised even in one per cent. aqueous solution.

THE EFFECT OF SUBSTITUENT GROUPS ON ROTATORY POWER

The substituent group arrange themselves in the following polar series deduced from their inductive capacities:

$$\overset{-}{OCH_3},\ OH,\ Cl,\ Br,\ I,\ CH_3,\ \overset{+}{H},\ COOH,\ CHO,\ COCH_3,\ CN,\ \overset{+}{NO_2}$$

(*a*) Ortho-*Substitution*.—On comparing the values of $[M]_{5461}^{35°}$ in water (Table III) it is found that CH_3, COOH, Cl, OH, I and OCH_3 groups cause an increase in the rotatory power in the following order:

$$OCH_3 > OH > I > COOH > Cl > CH_3 > H.$$

Thus all the groups except COOH behave in the same sense in conformity with the abovementioned polar series.

In methyl alcohol it is found that the substituent groups CH_3, Cl, OH, and OCH_3 cause a decrease in the value, while I, NO_2 and COOH cause an

TABLE III

$[M]^{35°}_{5461}$

No.	Camphor-β-sulphonate of	Water	Methyl alcohol	Ethyl alcohol	Pyridine
1	Aniline[a] ..	66·63 (3·400)[f]	105·3 (6·284)[f]	118·3 (6·997)[f]	123·8 (7·570)[f]
2	*o*-Toluidine[a] ..	67·36 (3·367)	100·3 (5·685)	117·8 (6·880)	122·8 (7·930)
3	*o*-Chloroaniline[b] ..	68·21 (3·078)	96·94 (4·251)	104·2 (5·058)	116·9 (5·379)
4	*o*-Iodaniline[c] ..	85·70 (3·110)	128·5 (5·254)	144·3 (6·037)	162·4 (7·216)
5	*o*-Aminobenzoic acid[d] ..	75·65 (3·560)	112·6 (5·950)	119·9 (6·270)	132·8 (7·123)
6	*o*-Nitroaniline[e] ..	..	110·9 (3·793)	109·1 (3·666)	118·2 (4·051)
7	*o*-Aminophenol ..	86·96 (4·706)	95·50 (5·364)	..	114·2 (6·650)
8	*o*-Anisidine ..	88·74 (4·774)	95·85 (5·144)	..	106·5 (5·614)
9	*m*-Toluidine[a] ..	63·74 (3·310)	97·97 (5·661)	115·6 (6·790)	120·3 (7·740)
10	*m*-Chloroaniline[b] ..	71·90 (3·644)	115·0 (6·386)	122·3 (6·945)	123·9 (6·541)
11	*m*-Iodaniline[c] ..	90·20 (3·268)	126·3 (5·195)	148·8 (6·122)	155·6 (6·917)
12	*m*-Aminobenzoic acid[d] .	71·94 (3·355)	107·0 (5·697)	110·7 (5·618)	127·3 (6·953)
13	*m*-Nitroaniline[e] ..	..	127·6 (5·882)	130·9 (5·432)	133·1 (5·185)
14	*m*-Anisidine ..	92·30 (5·072)	117·1 (7·324)	..	117·1 (6·173)
15	*p*-Toluidine[a] ..	68·48 (3·390)	103·3 (5·960)	120·3 (6·950)	127·5 (7·810)
16	*p*-Chloroaniline[b] ..	68·23 (3·510)	113·2 (6·276)	120·4 (6·689)	129·4 (6·420)
17	*p*-Iodaniline[c] ..	83·45 (3·207)	133·0 (5·357)	148·8 (6·310)	157·9 (7·077)
18	*p*-Aminobenzoic acid[d] ..	73·79 (3·475)	99·63 (5·113)	114·4 (5·777)	131·0 (7·139)
19	*p*-Nitroaniline[e] ..	..	112·7 (4·536)	112·6 (4·195)	116·2 (4·782)
20	*p*-Aminophenol ..	107·4 (5·958)	116·0 (6·592)	..	114·2 (6·650)
21	*p*-Anisidine ..	97·61 (5·139)	113·6 (7·660)	..	106·5 (5·694)

(*a*) Singh, B. K., *et al.*, *Proc. Lahore Phil. Soc.*, 1944, **6**, 15.
(*b*) ——— and Perti, O. N., *Proc. Ind. Acad. Sci.* (A), 1945, **22**, 265.
(*c*) ——— and Manhas, K. M. S., *Ibid.*, 1949, **29**, 107.
(*d*) ——— and Manhas, K. M. S., *Ibid.*, 1948, **27**, 1.
(*e*) ——— and Perti, O. N., *Ibid.*, 1945, **22**, 84.
(*f*) Values in brackets refer to "absolute" specific rotation constants (K_os).

increase. The order is $I > COOH > NO_2 > H > CH_3 > Cl > OCH_3 >$ OH. This agrees with the abovementioned polar series in the reverse sense with minor variations. In ethyl alcohol the groups CH_3, Cl and NO_2 cause a decrease in the value, while I and COOH cause an increase. The order is thus as follows:

$$I > COOH > H > CH_3 > NO_2 > Cl.$$

This does not agree with the abovementioned polar series.

On comparing the values of $[M]^{35°}_{5461}$ in pyridine, it is found that the order of decreasing rotatory power is $I > COOH > H > CH_3 > NO_2 > Cl > OH > OCH_3$. This also does not agree with the above polar series.

(*b*) Meta-*substitution*.—On comparing the values in water the order of decreasing rotatory power is $OCH_3 > I > COOH > Cl > H > CH_3$.

The order agrees with the abovementioned polar series in the same sense except for COOH and CH_3.

In methyl alcohol the order is

$$NO_2 > I > OCH_3 > Cl > COOH > H > CH_3.$$

The order does not agree with the abovementioned polar series.

In ethyl alcohol the order is

$$I > NO_2 > Cl > H > CH_3 > COOH$$

This again does not agree with the abovementioned polar series.

In pyridine the order is $I > NO_2 > COOH > Cl > H > CH_3 > OCH_3$.

The order does not at all agree with the abovementioned polar series.

(*c*) Para-*substitution*.—

The order in water is

$$OH > OCH_3 > I > COOH > CH_3 > Cl > H.$$

and agrees in the same sense with the above polar series with minor variations.

In methyl alcohol the order is

$$I > OH > OCH_3 > Cl > NO_2 > H > CH_3 > COOH.$$

This sequence does not agree with the abovementioned polar series.

In pyridine the order is

$$I > COOH > Cl > CH_3 > H > NO_2 > OH > OCH_3.$$

TABLE IV

Ortho-*anisidinocamphor-β-sulphonate*

Solvent	Water		Methyl alcohol		Pyridine		Chloroform	
Conc.	1·00%		1·00%		1·00%		1·00%	
Calculated $\begin{cases}[\alpha] \\ \lambda_0\end{cases}$	$\frac{4\cdot774}{\lambda^2-0\cdot1061}$ 0·3250		$\frac{5\cdot144}{\lambda^2-0\cdot1100}$ 0·3317		$\frac{5\cdot614}{\lambda^2-0\cdot1099}$ 0·3316		$\frac{6\cdot304}{\lambda^2-0\cdot1001}$ 0·3164	
Line	*d*-	*l*-	*d*-	*l*-	*d*-	*l*-	*d*-	*l*-
Li_{6703} ..	14·00	14·00	15·00	15·00	16·00	16·00	18·00	18·00
Cd_{6438} ..	15·00	15·50	16·75	16·75	18·00	18·50	20·00	20·00
Li_{6104} ..	18·00	18·00	19·50	19·00	21·50	21·50	23·00	23·00
Na_{5893} ..	19·75	19·75	21·50	21·50	23·50	23·50	25·25	25·25
Hg_{5780} ..	21·00	21·00	23·00	23·00	25·00	25·00	27·00	27·00
Hg_{5461} ..	25·00	25·00	27·00	27·25	30·00	29·75	32·00	31·75
Ag_{5209} ..	29·00	29·00	31·75	32·00	34·75	34·75	36·75	37·00
Cd_{5085} ..	31·00	31·00	34·25	34·25	38·00	38·00	39·75	39·75
Cd_{4800} ..	38·50	38·00	42·50	42·50	46·50	46·50	48·50	48·50
Cd_{4678} ..	42·25	42·75	47·00	47·60	51·50	51·75	53·00	53·00
Li_{4603} ..	45·00	45·00	50·50	50·50	57·00	57·00	56·50	56·50
Hg_{4358} ..	57·00	57·00	64·00	64·00	70·50	70·50	70·50	70·00

TABLE V

Meta-*anisidinocamphor-β-sulphonate*

Solvent	Water		Methyl alcohol		Pyridine		Chloroform	
Conc.	1·00%		1·00%		1·00%		1·00%	
Calculated $\begin{cases}[\alpha]\\ \lambda_0\end{cases}$	$\frac{5\cdot072}{\lambda^2-0\cdot1019}$ 0·3192		$\frac{7\cdot324}{\lambda^2-0\cdot0625}$ 0·2761		$\frac{6\cdot173}{\lambda^2-0\cdot1099}$ 0·3316		$\frac{6\cdot625}{\lambda^2-0\cdot1036}$ 0·3218	
Line	*d*-	*l*-	*d*-	*l*-	*d*-	*l*-	*d*-	*l*-
Li_{6708} ..	14·50	14·50	19·50	19·50	18·25	18·25	19·50	19·50
Cd_{6438} ..	16·25	16·25	21·25	21·25	20·25	20·25	21·75	21·00
Li_{6104} ..	18·75	18·75	25·00	24·50	23·50	23·50	23·50	23·75
Na_{5893} ..	20·75	20·75	27·00	27·00	26·00	26·00	27·00	27·00
Hg_{5780} ..	22·00	21·75	28·50	28·50	27·50	27·50	29·50	29·50
Hg_{5461} ..	26·00	25·75	33·00	33·00	33·00	32·75	34·25	34·25
Ag_{5209} ..	30·00	30·00	38·00	38·00	38·25	38·25	39·50	39·50
Cd_{5086} ..	32·50	32·50	40·00	40·50	41·50	42·00	42·50	42·50
Cd_{4800} ..	38·50	39·00	47·00	47·00	51·50	51·50	invisible	
Cd_{4678} ..	43·25	43·50	52·00	52·00	56·50	57·00	57·00	57·50
Li_{4603} ..	46·25	46·25	54·00	54·00	60·50	60·75	61·00	61·00
Hg_{4358} ..	invisible		64·50	64·50	78·50	77·50	77·00	77·50

TABLE VI

Para-*anisidinocamphor-p-sulphonate*

Solventt	Water		Methyl alcohol		Pyridine		Chloroform	
Conc.	1·00%		1·00%		1·00%		1·00%	
Calculated $\begin{cases}[\alpha] \\ \lambda_0\end{cases}$	$\frac{5\cdot139}{\lambda^2-0\cdot1102}$ 0·3320		$\frac{7\cdot660}{\lambda^2-0\cdot0587}$ 0·2423		$\frac{5\cdot694}{\lambda^2-0\cdot1073}$ 0·3276		$\frac{6\cdot434}{\lambda^2-0\cdot1021}$ 0·3196	
Line	*d*-	*l*-	*d*-	*l*-	*d*-	*l*-	*d*-	*l*-
Li_{6708} ..	15·00	15·50	19·50	19·50	16·50	16·00	18·50	18·50
Cd_{6438} ..	17·00	17·50	21·50	21·50	18·50	18·50	20·50	20·00
Li_{6104} ..	19·50	19·00	24·50	25·00	21·50	22·00	26·25	26·25
Na_{5893} ..	21·50	21·00	25·50	25·00	23·75	23·75	26·25	26·25
Hg_{5780} ..	23·00	23·00	28·00	28·50	25·00	24·00	27·25	27·25
Hg_{5461} ..	27·50	28·00	32·00	32·00	30·00	30·50	32·50	32·00
Ag_{5209} ..	32·75	33·00	36·00	36·00	34·75	34·75	38·00	38·00
Cd_{5086} ..	35·50	35·00	38·25	38·25	37·50	37·00	40·50	40·50
Cd_{4800} ..	42·50	42·00	44·00	43·00	46·25	46·25	50·00	49·50
Cd_{4678} ..	47·00	48·00	48·00	49·00	48·75	48·75	53·00	53·50
Li_{4603} .	50·50	50·00	50·00	50·00	54·50	54·50	58·00	57·50
Hg_{4358} ..	64·00	63·00	58·50	59·00	69·00	69·50	73·50	73·50

TABLE VII

Ortho-*aminophenol-camphor-β-sulphonate*

Solvent	Water		Methyl alcohol		Pyridine		Chloroform	
Conc.	1·00%		1·00%		1·00%		1·00%	
Calculated $[\alpha]$	$\frac{4\cdot706}{\lambda^2-0\cdot1125}$		$\frac{5\cdot364}{\lambda^2-0\cdot1055}$		$\frac{6\cdot650}{\lambda^2-0\cdot1015}$		$\frac{13\cdot01}{\lambda^2-0\cdot0989}$	
Calculated λ_0	0·3354		0·3248		0·3186		0·3145	
Line	*d-*	*l-*	*d-*	*l-*	*d-*	*l-*	*d-*	*l-*
Li_{6708} ..	13·75	13·75	15·50	15·50	21·00	21·00	37·50	37·50
Cd_{6438} ..	15·25	15·25	17·50	17·50	23·50	23·50	41·50	42·00
Li_{6104} ..	17·75	17·75	20·25	20·25	24·50	24·50	48·00	48·00
Na_{5893} ..	19·75	19·75	22·25	22·25	27·00	27·00	53·00	53·00
Hg_{5780} ..	21·00	21·00	23·50	23·50	28·50	28·50	56·00	56·00
Hg_{5461} ..	25·50	25·50	28·00	28·00	33·50	33·50	66·00	66·00
Ag_{5209} ..	29·00	29·00	32·25	32·25	39·50	39·50	76·50	76·50
Cd_{5086} ..	31·50	31·50	35·00	35·00	42·25	42·00	82·50	82·50
Cd_{4800} ..	39·50	39·50	43·00	43·00	50·00	50·00	100·00	100·00
Cd_{4678} ..	43·50	43·50	47·50	47·50	56·50	56·50	109·50	109·50
Li_{4603} ..	46·50	46·50	50·50	50·50	62·00	62·00	116·50	116·05
Hg_{4358} ..	59·75	59·75	63·50	63·50	75·00	75·00	145·00	145·00

TABLE VIII

Para-*aminophenol-camphor-β-sulphonate*

Solvent	Water		Methyl Alcohol		Pyridine		Chloroform	
Conc.	1·00%		1·00%		1·00%		1·00%	
Calculated $[\alpha]$	$\frac{5\cdot958}{\lambda^2-0\cdot1089}$		$\frac{6\cdot592}{\lambda^2-0\cdot1075}$		$\frac{6\cdot650}{\lambda^2-0\cdot1015}$		$\frac{7\cdot074}{\lambda^2-0\cdot1114}$	
Calculated λ_0	0·3300		0·3279		0·3186		0·3338	
Line	*d*-	*l*-	*d*-	*l*	*d*-	*l*-	*d*-	*l*-
Li_{6708} ..	17·50	17·00	19·25	20·00	19·00	19·00	21·00	21·00
Cd_{6438} ..	19·50	19·50	20·50	20·50	21·50	21·50	23·50	23·50
Li_{6104} ..	22·50	22·50	26·00	26·00	24·50	24·50	27·00	27·00
Na_{5893} ..	25·00	25·00	27·50	27·50	27·00	27·00	30·00	30·00
Hg_{5780} ..	26·50	26·50	29·00	29·00	28·75	28·50	31·75	32·00
Hg_{5461} ..	31·50	31·50	34·00	34·00	33·50	33·50	36·00	36·00
Ag_{5209} ..	36·50	36·50	40·25	40·00	39·50	39·50	44·00	44·00
Cd_{5086} ..	40·00	40·00	43·50	43·00	42·25	42·25	48·00	48·00
Cd_{4800} ..	49·00	49·00	53·50	53·50	52·00	52·00	59·50	59·50
Cd_{4678} ..	54·00	54·00	59·25	59·00	56·50	56·50	65·50	65·50
Li_{4603} ..	58·00	58·50	63·00	63·00	62·00	62·00	70·50	70·50
Hg_{4358} ..	73·50	73·50	80·00	80·00	75·00	75·00	90·00	90·00

The groups I, Cl, CH_3 and COOH cause an increase in the rotatory power and the groups OH, NO_2 and OCH_3 cause a decrease in rotatory power. This is in conformity with the above mentioned polar series except in the case of COOH, OH and OCH_3 groups.

THE EFFECT OF POSITION ISOMERISM ON ROTATORY POWER

In Table IX the order of rotatory power, $[\alpha]_{\lambda}^{35°}$, of isomeric anisidinocamphor-β-sulphonates is given:

TABLE IX

Solvent	$[\alpha]_D^{35°}$
Water ..	*p* > *m* > *o* > *un* [*p* > *m* > *o* > *un*]
Methyl alcohol ..	*m* > *un* > *p* > *o* [*p* > *m* > *un* > *o*]
Pyridine ..	*un* > *m* > *p* > *o* [*un* > *m* > *p* > *o*]
Chloroform ..	*un* > *m* > *p* > *o* [*un* > *m* > *p* > *o*]

The order of $k_o s$ is also given in brackets. On comparing the values of $[\alpha]_D^{35°}$ in different solvents it is found that the decreasing order of specific rotatory power does not agree with Frankland's[3] "lever arm" hypothesis or its electrostatic modification as suggested by Rule.[4] Comparison of the decreasing order of $k_o s$ also does not show any agreement with the "lever arm" hypothesis of Frankland[3] except in methyl alcohol.

In Table X are recorded the decreasing order of the specific rotatory powers, $[\alpha]_D^{35°}$, of the position isomers of aminophenolcamphor-β-sulphonates in different solvents. The decreasing order of the rotation constants, $k_o s$, are also given in brackets.

TABLE X

Solvent	$[\alpha]_D^{35°}$
Water ..	*p* > *o* > *un* [*p* > *o* > *un*]
Methyl alcohol ..	*p* > *un* > *o* [*p* > *un* > *o*]
Pyridine ..	*un* > *o* = *p* [*un* > *o* = *p*]
Chloroform ..	*o* > *un* > *p* [*o* > *un* > *p*]

Here we find that the sequence is in agreement with the Frankland's "lever arm" hypothesis[3] and its electrical modification as suggested by Rule[4] in methyl alcohol and chloroform. The *meta*-isomers are not investigated as yet, and this agreement is, therefore, subject to this fact.

Experimental

Camphor-β-sulphonates (*d*-, *l*-, and *dl*-) of *o*-, *m*- and *p*- *anisidine* and *o*- and *p-aminophenol.* Molecular proportions of the amines and the acids were separately dissolved in ethyl acetate and on mixing the two solutions, the salts crystallised out. They were repeatedly recrystallised from absolute ethyl alcohol as fine white needles. They are very soluble in pyridine and water, less so in methyl alcohol, chloroform and ethyl alcohol and insoluble in acetone and benzene.

Anisidinocamphor-β-Sulphonates

Ortho-salts:

d-form, m.p. 153° C.; S, 9·2%.

l-form, m.p. 153° C.; S, 9·2%.

dl-form, m.p. 171° C.; S, 9·2%.

Meta-salts:

d-form, m.p. 103° C.; S, 8·0%.

l-form, m.p. 103° C.; S, 8·9%.

dl-form, m.p. 161° C.; S, 8·9%.

Para-salts:

d-form, m.p. 159° C.; S, 8·8%.

l-form, m.p. 159° C.; S, 8·8%.

dl-form, m.p. 170° C.; S, 9·2%.

$C_{17}H_{25}O_6NS$ requires S, 9·0%.

Aminophenolcamphor-β-Sulphonates

Ortho-salts:

d-form, m.p. 165° C.; S, 9·5%.

l-form, m.p. 165° C.; S, 9·0%.

dl-form, m.p. 170° C.; S, 9·1%.

Para-salts:

d-salt, m.p. 151° C.; S, 9·12%.

l-salt, m.p. 151° C.; S, 9·45%.

dl-salt, m.p. 172° C.; S, 9·2%.

$C_{16}H_{25}O_6NS$ requires S, 9·35%.

The rotatory power determinations were carried out in a 2- dcm-jacketed tube at 35° C. (Tables IV to VIII). The values λ_0, calculated from the dispersion formulæ, are given in these tables and are expressed as μ or 10^{-4} cm.

Summary

1. The rotatory dispersion of stereoisomeric salts of *o*-, *m*- and *p*-anisidine and *o*- and *p*-amino-phenols with camphor-β-sulphonic acid (*d*- and *l*-) is found in different solvents to obey Drude's one-term equation, $[\alpha]=\frac{k_0}{\lambda^2-\lambda_0{}^2}$; it is, therefore, " Simple ".

2. The *d*- and *l*-forms of these compounds possess identical rotatory power and thus support Pasteur's Law of Molecular Dissymmetry.

3. The sequence of rotatory power in different solvents is in the reverse order of their dielectric constants with minor variations.

4. The racemic forms of the salts are found to be true *dl*-compounds.

5. The influence of hydroxy and methoxy groups on the rotatory power is discussed.

6. The effect of position isomerism on rotatory power has also been discussed.

Acknowledgement

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SULPHANILAMIDES

Part II. *In vitro* Synergism with Anionic Surface-Active Compounds

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Combined administration of two or more drugs in the chemotherapy of severe infections has frequently shown synergistic effects, permitting the use of smaller doses of each compound and preventing or reducing toxic effects and reactions.[1–5] Successful treatment of mixed infections and prevention of acquired drug resistance by micro-organisms are also possible.[6–7] These observations have been made on sulphanilamides and antibiotics such as penicillin and streptomycin.[8–9]

Surface-active compounds of certain types inhibit bacterial metabolism in high dilutions,[10–14] and they have been used largely to increase the potency of germicidal and disinfecting agents.[15–18] There are a few recent reports concerning their synergism with chemotherapeutics.[19–21] The low solubilities of sulpha drugs, the high concentrations needed for bacteriostatic action in natural habitats in comparison with penicillin and similar antibiotics and, in particular, the rapid development of resistance by most micro-organisms make it desirable to use them in combination with other antibacterial agents. This study on the additive bacteriostatic effects *in vitro* of certain surface-active compounds and sulpha drugs was therefore undertaken as part of investigations in progress[22] on the synthesis of compounds possessing antibacterial action and surface activity.

The recognition that conventional peptone media contain sulphanilamide inhibitors obscuring the complete manifestation of potential drug activity[23–25] has led to the use of various synthetic media,[26–29] although the latter are obviously less suitable for bacteriostatic studies on the basis of which *in vivo* tests are to be planned. Both synthetic and peptone media have been employed in the present work.

Methods

Bacteriological tests were carried out against *Staphylococcus aureus* Rosenbach, *Escherichia coli* (Migula) Castellani and Chalmers, and *Eberthella typhosa* (Zopf) Weldin. The culture media used were nutrient broth (Stearn's peptone, 1 per cent.; beef extract Lab. Lemco, Oxo, 0·4 per cent.; and sodium chloride, 0·5 per cent.) and the synthetic medium[29] of Muir, *et al.*

($NH_4H_2PO_4$, 0·1 per cent.; K_2HPO_4, 0·1 per cent.; sodium citrate 0·2 per cent.; $MgSO_4$, 0·02 per cent.; and NaCl, 0·5 per cent.), both at pH 7·6. The media were tubed in 5 c.c. quantities and stock slants of the test organisms were maintained on 2 per cent. agar with the respective media through fortnightly transfers. Test cultures were transplanted into the media and incubated at 37°. The organisms grew well in the artificial medium only after a period of adaptation by repeated subculturings (*cf.* ref. 28).

Since young cultures, during their logarithmic phase of growth, are more susceptible to drug action than the cells from older cultures,[28, 30, 31] 16–18 hour cultures of the organisms were employed for the tests unless otherwise stated.

The inoculum for the tests consisted of cells grown in the medium to be used and washed twice by centrifugation in the same medium; water, saline, or buffer was not used for washing since they were likely to kill or injure some of the cells. The size of the inoculum was normally a 2 mm. loopful from a standard suspension which gave the same density in a Klett-Summerson photo-colorimeter and corresponded to 5,000–10,000 cells. A small variation, not allowed for, in the volume of medium carried by the standard loop is likely to have been caused by the alterations in surface tension brought about by the surface-active agents where present.

The drugs tested were sulphanilamide, sulphadiazine, sulphapyridine, sulphathiazole, sulphamerazine, and sulphaguanidine. The surface-active agents used were Igepon T (General Dyestuffs), sodium salt of N-oleyl N-methyltaurine; Aerosol OT (American Cyanamid), sodium dioctyl sulphosuccinate and Nekal BX (I.G. Farbenindustrie), sodium salt of a dibutylnaphthalenesulphonic acid. The drug or the surface-active compound to be tested was incorporated into the medium prior to tubing and, where necessary (as with certain of the sulpha drugs), a minimal amount of dilute hydrochloric acid was employed to facilitate solution of the drug, the pH being maintained at 7·6 ±0·2; there was no precipitation of the surface-active compound. Bacteriostasis was determined on the basis of the absence of visible growth at the end of 72 hours unless specified otherwise.

Effects of age of culture, size of inoculum and temperature.—Since time and temperature of incubation and number of bacteria inoculated, in addition to the type of medium, are important factors, which may influence the conclusions drawn from sulphanilamide studies *in vitro*,[31, 32] these were ascertained in the following experiments. Eighteen and 24-hour old cultures of *S. aureus* in peptone-broth and synthetic media were used as inocula in final dilutions of (*a*) 1 in 50, (*b*) 1 in 2,500, (*c*) 1 in 1,25,000 and (*d*) 1 in 6,250,000. A standard loopful of the undiluted culture in 5 c.c. of the medium corresponded approximately to a dilution of 1 in 250. Dilution (*d*) was

not employed with the synthetic medium. Observations for visible growth in presence of varying amounts of sulphanilamide were made at different time intervals after incubation at 37° and at 43°. The results are shown in Table I.

TABLE I

Effect of age of culture on the susceptibility of S. aureus *to sulphanilamide in relation to temperature and dilution*

Hours' incubation	Dilution of inoculum	Concentration of sulphanilamide (mg. per cenr)							
		Nil (control)		400		600		800	
Temp. of incubation		37°	43°	37°	43°	37°	43°	37°	43°
(i) Culture 24 hours : Peptone-broth medium									
16	a	+	−	+	±	−	−	−	−
	b	+	−	−	−	−	−	−	−
	c	−	−	−	−	−	−	−	−
	d	−	−	−	−	−	−	−	−
24	a	++	+	+	+	+	−	−	+
	b	++	+	±	−	+	−	−	+
	c	+	+	−	−	−	−	−	−
	d	+	+	−	−	−	−	−	−
48	a	++	++	++	++	+	+	+	−
	b	++	++	++	+	+	−	+	−
	c	+	+	+	−	+	−	±	−
	d	+	+	+	−	+	−	−	−
72	a	++	++	++	++	++	++	++	−
	b	++	++	++	+	++	+	+	−
	c	++	++	++	+	++	+	+	−
	d	++	++	+	+	++	−	+	−
(ii) Culture 18 hours : Peptone-broth medium									
16	a	+	−	−	−	−	−	−	−
	b	+	−	−	−	−	−	−	−
	c	−	−	−	−	−	−	−	−
	d	−	−	−	−	−	−	−	−
24	a	++	+	−	−	−	−	−	−
	b	++	+	−	−	−	−	−	−
	c	+	+	−	−	−	−	−	−
	d	+	+	−	−	−	−	−	−
48	a	++	++	+	±	+	+	+	−
	b	++	++	+	−	+	−	−	−
	c	++	++	−	−	−	−	−	−
	d	++	++	−	−	−	−	−	−
72	a	++	++	++	+	+	+	+	−
	b	++	++	±	+	+	+	+	−
	c	++	++	−	−	−	−	±	−
	d	++	++	−	−	−	−	−	−

TABLE I—(*Contd.*)

Hours' incubation	Dilution of inoculum	Concentration of sulphanilamide (mg. per cent.)							
		Nil (control)		400		600		800	
Temp. of incubation		37°	43°	37°	43°	37°	43°	37°	43°
		(iii) Culture 24 hours : synthetic medium							
16	a	+	+	+	−	−	−		
	b	+	+	+	±	−	−		
	c	−	−	−	−	−	−		
24	a	+	+	+	+	−	−		
	b	+	+	±	+	−	−		
	c	+	+	−	−	−	−		
48	a	++	++	++	++	−	−		
	b	++	++	++	++	−	−		
	c	++	++	++	++	−	−		
72	a	++	++	++	++	+	−		
	b	++	++	++	++	−	−		
	c	++	++	++	++	−	−		
		(iv) Culture 18 hours : synthetic medium							
16	a	+	+	+	±	−	−		
	b	+	+	+	−	−	−		
	c	+	+	−	+	−	−		
24	a	+	+	+	±	−	−		
	b	+	+	+	+	−	−		
	c	+	+	+	+	−	−		
48	a	++	++	++	++	−	−		
	b	++	++	++	++	−	−		
	c	++	+	++	++	−	−		
72	a	++	++	++	+	−	−		
	b	++	++	++	++	−	−		
	c	++	++	++	++	−	−		

− No growth. + Definite but small growth.
± Traces of growth. ++ Good to maximum growth.

With the peptone medium generally, the older the cells and the lower the temperature of incubation the less susceptible is the organism to the drug. The results at the higher temperature are relatively independent of the age of the culture and the concentration of the inoculum. With the synthetic medium, on the other hand, the effects of age of culture and size of inoculum are less pronounced at either temperature. The explanation

for this observation might be that, owing to the more steady and prolonged growth of the organism in the peptone-broth medium, the cells used in the different inocula vary somewhat in their stages of growth. Rose and Fox[33] consider that the bacterial cell contains a susbtance necessary for reproduction which is synthesized normally but not in presence of bacteriostatic concentrations of sulphanilamides. This would imply that with heavy inocula there is no bacteriostasis with the same effective concentration of drug as with more dilute inocula. Neter[34] has reported that the number of organisms in the inoculum does not affect the drug concentration needed for growth inhibition, provivded the studies are carried out at higher incubation temperatures.

In the following studies, the incubation temperature employed was normally 43° for the peptone-broth medium and 37° for the synthetic medium.

Minimum effective concentrations of sulpha drugs and surface-active compounds.—The results of antibacterial titre tests with the drugs and the wetting agents are given respectively in Tables II and III.

TABLE II

Minimum inhibitory concentrations of sulpha drugs

Sulpha drug	Organism	Synthetic medium		Peptone broth medium	
		37°	43°	37°	43°
		(mg. per cent)			
Sulphanilamide	*S. aureus* ..	600	600	900	800
	E. coli ..	500	600	600	600
	E. typhosa ..	500	500	750	800
Sulphadiazine	*S. aureus* ..	22	20	200	300
	E. coli ..	20	15	300	400
	E. typhosa ..	15	15	300	300
Sulphapyridine	*S. aureus* ..	20	18	300	300
	E. coli ..	22	20	500	500
	E. typhosa ..	18	15	400	400
Sulphathiazole	*S. aureus* ..	15	20	300	200
	E. coli ..	15	15	450	400
	E. typhosa ..	20	20	300	400
Sulphamerazine	*S. aureus* ..	45	40	400	300
	E. coli ..	40	45	400	400
	E. typhosa ..	40	45	400	400
Sulphaguanidine	*S. aureus* ..	300	250	300	300
	E. coli ..	300	250	250	200
	E. typhosa ..	400	400	300	200

TABLE III

Minimum inhibitory concentrations of surface-active compounds

Culture: *S. aureus*: 18 hrs., pH 7·6

Surface-active compound	Synthetic medium		Peptone medium	
	37°	43°	37°	43°
Temp. of incubation	mg. per cent.			
Nekal BX ..	12	12	10	12
Igepon T ..	20	30	24	30
Aerosol OT ..	5	8	24	30

No growth inhibition was observed against *E. coli* and *E. typhosa* with concentrations of surface-active agents less than 40 mg. per cent. in the synthetic medium and less than 200 mg. per cent. in the nutrient broth medium; higher concentrations were not tried. This is in accordance with the experience that anionic sufrace-active compounds of the usual type selectively inhibit the metabolism of Gram-positive organisms only.[35, 11]

As may be expected, greater amounts of the sulpha drugs are needed in peptone-broth medium than in the synthetic medium. This is also true of the surface-active compounds, especially Aerosol OT, against *S. aureus*. The interference due to peptone in the evaluation of detergents as disinfectants has been shown by others[36, 37, 14]; this may in part be due to phospholipids in peptone preparations which are known to neutralize the bacteriostatic activities of surface-active compounds.[38]

Differences between the drugs are also brought out better in the synthetic medium. There are variations in the order of their efficiencies at the two temperatures, in the two media and with the three organisms. Higher titres are needed against *E. coli* and *E. typhosa*.

While the concentration of drug for growth inhibition of the different organisms is more or less the same at the two temperatures of incubation, somewhat higher amounts of the surface-active compounds are needed at the higher temperature. With the rather limited data, no simple explanation is possible for this observation.

Synergistic effects of sulpha drugs and surface-active compounds.—With *S. aureus*, the wetting agents were employed in dilutions which in them-

selves were not bacteriostatic. The organism was then titrated against the sulpha drugs to ascertain the minimal concentrations for growth inhibition (Table IV). Synergism was inferred if the concentrations of the drugs were

TABLE IV

Synergism between sulpha drugs and surface-active compounds

Organism: *S. aureus*

Sulpha drug	Peptone-broth medium			Synthetic medium		
	Nekal BX 8 mg. %	Igepon T 20 mg. %	Aerosol OT 20 mg. %	Nekal BX 6 mg. %	Igepon T 10 mg. %	Aerosol OT 3 mg. %
	Milligrams per cent.					
Sulphanilamide	800*	800*	400	400	450	450
Sulphadiazine	100	100	20	10	10	12
Sulphapyridine	80	100	300*	15	10	15
Sulphathiazole	100	80	60	12·5	10	12·5
Sulphamerazine	100	80	20	30	25	35
Sulphaguanidine	300*	300*	300*	300*	250	300*

* No synergistic effect in these cases.

less than those given in Table II. With *E. coli* and *E. typhosa*, titrations were carried out against the surface-active compounds using sub-minimal amounts of the sulpha drugs. Some of the best combinations obtained for bacteriostasis are reported in Tables V and VI respectively.

TABLE V

Synergism between sulpha drugs and surface-active compounds

Organism: *E. coli*

Sulpha drug	Peptone-broth medium			Synthetic medium		
	Nekal BX	Igepon T	Aerosol OT	Nekal BX	Igepon T	Aerosol OT
	Milligrams per cent.					
Sulphanilamide	400+60	400+120	..	200+20	300+30	300+20
Sulphadiazine	300+40	200+ 80	300+80	12+20	12+25	10+30
Sulphapyridine	400+20	200+ 40	300+40	10+25	15+30	15+40
Sulphathiazole	200+20	100+ 40	200+40	10+20	12+30	12+20
Sulphamerazine	300+20	200+ 40	300+40	30+25	30+25	*
Sulphaguanidine	*	200+ 80	*	250+20	200+50	*

Figures in columns refer to sulpha drug and surface-active compound respectively.

* No synergism in these cases.

TABLE VI

Synergism between sulpha drugs and surface-active compounds

Organism: *E. typhosa*

Sulpha drug	Peptone-broth medium			Synthetic medium		
	Nekal BX	Igepon T	Aerosal OT	Nekal BX	Igepon T	Aerosol OT
	Milligrams per cent.					
Sulphanilamide ..	600+40	400+80	600+ 80	300+20	400+20	400+30
Sulphadiazine ..	200+40	200+80	200+ 80	12+20	12+25	12+20
Sulphapyridine ..	200+60	200+80	200+120	15+20	15+20	15+25
Sulphathiazole ..	200+20	100+40	100+ 40	15+30	15+20	10+20
Sulphamerazine ..	300+40	300+40	300+ 40	30+20	25+20	30+20
Sulphaguanidine ..	*	*	*	300+25	300+30	300+25

Figures in columns refer to sulpha drugs and surface-active compounds respectively.
* No synergism in these cases.

Tables IV–VI indicate marked synergism between drug and surface-active compound. This effect was least shown with sulphaguanidine, especially in peptone medium, against all the organisms. With the other sulpha compounds, the degree of synergism varied rather widely. While the surface-active compounds by themselves were ineffective against Gram-negative organisms, they had definite potentiating activity in conjunction with the sulpha drugs, the effect being more pronounced with peptone broth. The surface-active compounds apparently act both by facilitating drug penetration into the cell and by counteracting the natural sulphanilamide inhibitors. It has been demonstrated that Gram-negative micro-organisms can be sensitized to anionic surface-active compounds by means of protamine, possibly by its interaction with a natural inhibitory substance.[39] Munshi, *et al.*[22] have observed that under certain conditions surface-active anions might make a contribution to bacteriostasis by removing part of the essential metabolite, *p*-aminobenzoic acid, as a salt.

Additive effects of sulphanilamides and surface-active compounds on drug-fast organisms.—Resistant strains of *S. aureus* were obtained by successive transfers through increasing concentrations of sulphanilamide and sulphathiazole in peptone-broth medium. When tested against mixtures of sulphanilamide or sulphathiazole and Aerosol OT, growth inhibitions occurred at the same combined concentration of the two substances as with the original susceptible organism. Likewise, when *S. aureus* was grown in nutrient medium containing 0·2 per cent. of animal lecithin (Eastman Kodak) and

the cells washed and resuspended in nutrient broth before being used as inoculum, it was resistant to 30 mg. per cent. of Aerosol OT in nutrient medium (*cf.* ref. 38), but not to the same concentration of a mixture of sulphanilamide and Aerosol OT (Table IV) as the susceptible organism. Thus, resistance acquired to a sulpha drug or the inhibition of antibacterial effect of a surface-active compound is no longer manifested in presence of a combination of the two bacteriostatic agents. Treffers[40] has observed that a strain of *S. dysenteriae*, rendered resistant to penicillin, is not similarly resistant to a combination of penicillin and iodoacetic acid.

The present work has indicated that certain anionic surface-active compounds, besides potentiating the bacteriostatic properties of sulpha drugs, are effective against the acquirement of drug resistance. The effectiveness of the surface-active agents in combination with sulpha drugs against Gram-negative organisms would suggest that their bacteriostatic and surface-active properties are independent of each other. Whatever may be the mechanism of their synergising action, it would appear that, if non-toxic (*cf.* refs. 12, 41), they may find a place in sulphanilamide chemotherapy.

Summary

1. The bacteriostatic properties of sulphanilamide and five N^1-substituted sulphanilamides, and of three anionic surface-active compounds, have been studied, singly and together, against the organisms, *S. aureus*, *E. coli*, and *E. typhosa*, using peptone-broth and a synthetic medium.

2. With incubation temperatures of 37° and 43° the concentration of sulphanilamide for bacteriostasis in peptone medium is independent of the age of the culture and the concentration of the inoculum at the higher temperature only. In the synthetic medium, the effects of age of cells and size of inocula are less pronounced at both temperatures of incubation.

3. The minimum effective concentrations of sulpha drugs needed for growth inhibition are more in peptone broth than in the synthetic medium. Similar but less pronounced differences are seen with the surface-active compounds against *S. aureus*.

4. While the surface-active compounds are by themselves ineffective against the Gram-negative organisms, they have potentiating activity with the sulpha drugs.

5. The synergic effects of sulphanilamide and surface-active compound are unaltered even when the organism is rendered resistant to sulphanilamide or when the antibacterial property of the surface-active compound is neutralized by lecithin.

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REDUCTION PROCESSES AT THE DROPPING MERCURY ELECTRODE IN PULSATING FIELDS

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1. Introduction

Breyer and Gutmann[1] have obtained interesting results by studying the effect of a superimposed alternating field on the reversible depolarising process taking place at a dropping mercury electrode of the type used in polarography. Their experiments are related to systems involving the discharge of cadmium, thallium and zinc ions. All their experiments were conducted with an alternating current of 50 cycles per second. In the present work the discharge of lead ions has been studied by a similar technique varying the frequency from 12·5 to 600 cycles per second. Since the dropping mercury electrode is really being subjected to the combined action of a D.C. and an A.C. field, it is considered more appropriate to call the field acting as "pulsating" field.

2. Experimental

The circuit diagram used is given in Fig. 1. The source of alternating current was a B.S.R. oscillator capable of giving an output of any frequency from 0–16,000 cycles per second. The output of the oscillator was fed on to a potentiometer ACB which was used as a potential divider. The voltage output of the oscillator was adjusted to give a voltage of 32 r.m.s. millivolts between B and C. The D.C. voltage was got from two dry cells connected to a Cambridge pH potentiometer D (with the galvanometer shorted off) which was used as a potential divider. The output of the potentiometer between EF could be varied continuously, the resistance R 4 being 450 ohms per volt of direct current voltage. G was a Leeds and Northrup galvanometer of period 14·8 secs. and resistance 1,182 ohms. The shunt R 5 was 10 ohms. This arrangement gave a sensitiveness 5 mm./μA on the scale. A and H were connected to the X and Y input terminals respectively of a DuMont oscillograph type 208 B. B was connected to the common earth terminal. The Y-deflection gave a measure of the alternating current passing through the dropping electrode. The galvanometer G helped to measure

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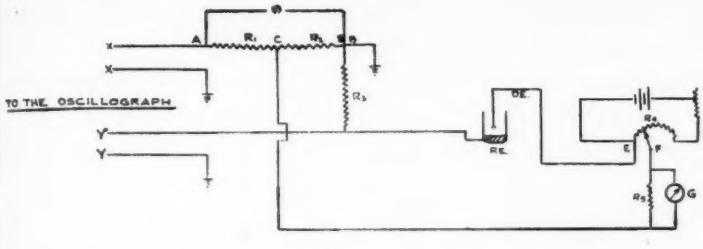
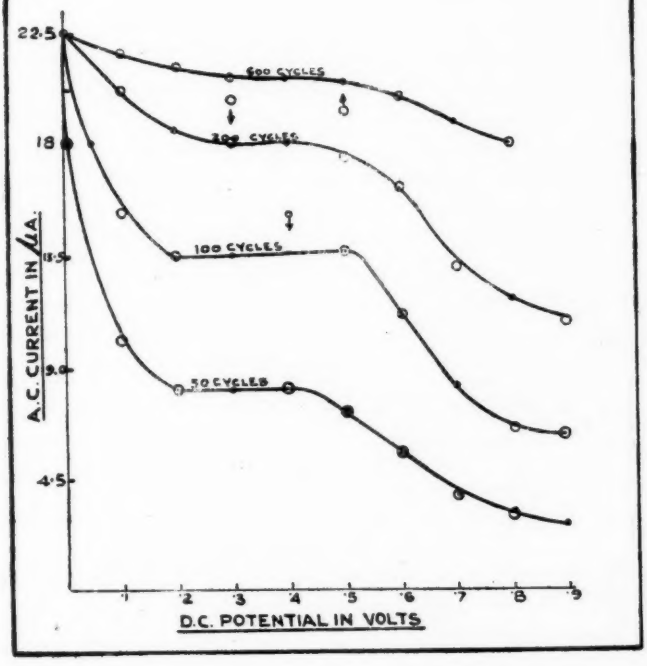


FIG. 1

D.E. = DROPPING ELECTRODE. P.E. = POOL ELECTRODE.
R_1 = 15840 Ω } FOR FREQUENCIES RANGING FROM
R_2 = 40 Ω } 50 ∿ TO 600 ∿ PER SEC.
R_3 = 1000 Ω.
R_4 = 450 Ω per volt
R_5 = 10 Ω.
R_6 = 150 Ω } FOR LOW FREQUENCIES
R_7 = 7 Ω } BELOW 50 ∿ PER SEC.

FIG. No. 2.

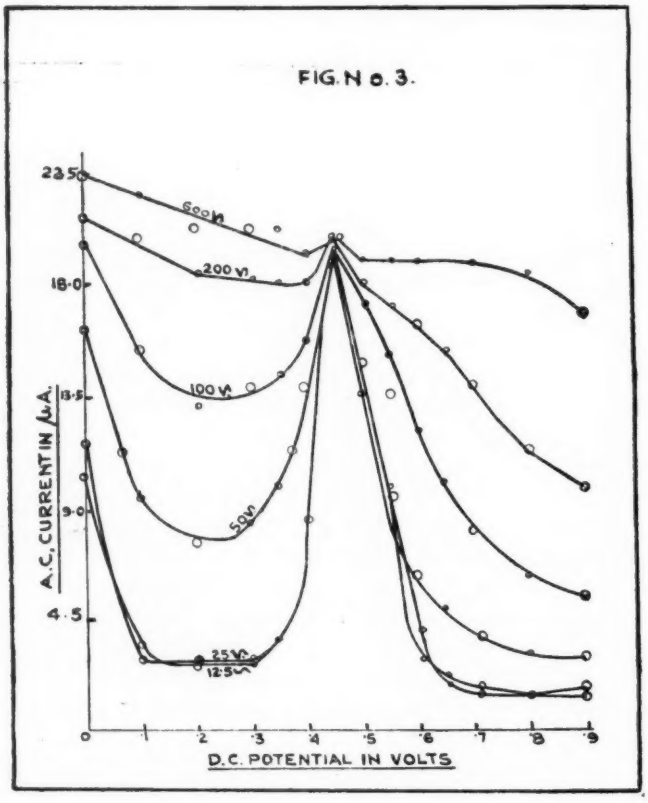


simultaneously the polarographic current at different applied D.C. voltages. The dropping electrode had the following characteristics:—

$m = 1 \cdot 27$ mg./sec. $t = 5 \cdot 1$ secs./drop; in distilled water in the open circuit.

First the experiment was performed with a molar aqueous solution of potassium chloride freed from air and containing no other dischargeable ions. The alternating current at various frequencies, passing through the dropping electrode system at various D.C. potentials was measured and the results are given in Fig. 2.

This experiment was repeated with the molar potassium chloride solution containing 2×10^{-3} M lead ions (added in the form of lead nitrate) and the results are given in Fig. 3. This solution was also air-free.



3. Discussion

(i) *Variation of A.C. current with applied D.C. voltage.*—The dropping mercury electrode system can be considered, for the purposes of its behaviour under the action of alternating fields, as consisting of a resistance and capacitance in series. When one is dealing with a mere solution of the indifferent electrolyte such as 1M- KCl, the capacitative impedance of the electric double layer at the dropping electrode is high. With increase in the frequency of the alternating field, the capacitative impedance diminishes. In the present case at about 600 cycles, the capacitative impedance becomes small as compared with the resistive impedance of the whole system, so that a further increase in frequency of the alternating field does not materially alter the current flowing through the system.

When an electro-reducible substance is present in the system and the dropping electrode is given a cathodic D.C. potential, the depolarising action of the electro-reducible substance brings about a fall in the impedance of the dropping electrode. This is due to the system behaving as if the condenser constituted by the electric double layer is being shorted by a resistance, the value of which diminishes with increasing depolarising action. This effect is maximum at the polarographic half-wave potential of the depositing ion. This could be clearly observed as simultaneous observations could be taken of the alternating current passing through the system as well as the polarographic current. Since the resultant impedance of the dropping electrode reaches a very low value at the half-wave potential even with the frequency of 12·5 cycles, any further rise of frequency of the field upto 600 cycles or more has only a small effect on the A.C. current passing through the system. This explains why the peak currents at the half-wave potential in Fig. 3 are all nearly of the same order and are nearly equal to the current obtained at high frequency at the same potential with a solution of 1 M-KCl.

At other D.C. potentials however, the capacitative impedance of the dropping electrode at 12·5 cycles is quite effective and therefore the current passing through the system is dependent on the frequency of applied alternating field.

The S-shaped curves in Fig. 2 are to be attributed to the combined effect of the D.C. potential on (*a*) the capacity of the electrical double layer at the dropping electrode, (*b*) the size of the drop due to the electrocapillary effect, and (*c*) the leaking effect due to the depolarising ions in the capacity of the electric double layer.

(ii) *Phase shifts brought about by the dropping electrode.*—The changes in the dropping electrode system brought about by the applied D.C.

potential have been visually demonstrated by observing the effect of those changes on the phase of the A.C. current, by making use of the oscillograph. The arrangement used by Randles[2] is no doubt the best especially for quantitative measurements. But since our oscillograph had a low amplification on the x-axis, a slightly different method has been employed to get a qualitative idea of the phase changes.

Fig. 1 shows the arrangement.

The phase shift as deduced from the ellipticity of the figures obtained on the oscillograph becomes smaller as the half-wave potential is reached. Similarly when the frequency of the alternating field increases the phase shift tends to diminish. These observations in general confirm the conclusions arrived at on the basis of the A.C. current D.C. potential curves, indicating a decrease in the overall capacitative impedance of the system, both as the half-wave potential is approached and as the A.C. frequency increases.

In view of the fact that the dropping mercury electrode at the half-wave potential of the reducible ion simulates the system dealt with by Randles[2] it should have been possible to interpret these results on the basis of his theory; but the alternating field applied is very large (32 millivolts, r.m.s.) and the approximation made in his formulation may not apply to the present case.

The authors wish to thank Shri S. C. Roy, Director, Indian Institute of Sugar Technology, Kanpur, for his kind interest in the work and the United Provinces Scientific Research Committee for a grant which made this work possible.

4. Summary

The work of Breyer and Gutmann on the effect of superimposing alternating fields on the reduction processes occurring at the dropping mercury electrode, has been extended to lead solutions. The work has been done at different frequencies of the alternating field. All the results obtained are interpretable on the basis of the diminution in the overall capacitative impedance of the dropping electrode as the half-wave potential is approached as well as when the frequency of the alternating field increases. These results are largely confirmed by direct observations on phase shifts by means of the oscillograph.

References

1. Breyer and Gutmann .. *Faraday Society Discussion*, 1947, No. 1, 19.
2. J. E. B. Randles .. *Ibid.*, p. 11.

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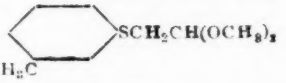
ERRATA

Proc. Ind. Acad. Sci., Vol. XXXII, Sec. A, No. 6

Part I. Page 394, In line 8 from top, the word "hydroazone" should be replaced by the word "hydrazone".

Part II. Page 396, 1st para, line 8, from top *for* 'thionaphthene.' *read* 'thionaphthenes.'

Page 397, In formula (III), shift CH_3 group to the left, so that it is *m*- to side chain. The correct representation is



Page 400, In line 18 from top, insert a '/' between "160–80°" and "110 mm." The correct representation is "160–80°/110 mm."